Optimization of Fungal Adsorption of Uranium

Final Report

June, 1988

for

Department of Supply and Services Canada
11C1, Place du Portage, Phase III
11 Laurier Street
Hull, Quebec
K1A 0S5

Attention: Mrs. A. Humphrey

Submitted by:

V.I. Lakshmanan
G. Heinrich
G.M. Freeman

Mineral Resources

ORF Account No. 40-10931
DSS Serial No. ~~14SQ.23440-6-9042~~ 03 7-9222

July 4, 1988

CONTRACT SERIAL NUMBER 79222-01-SQ
DSS REQUISITION NUMBER 23440-7-9222
CONTRACTOR: Ontario Research Foundation

ONTARIO RESEARCH FOUNDATION
SHERIDAN PARK RESEARCH COMMUNITY
MISSISSAUGA, ONTARIO, CANADA, L5K 1B3
(416) 822-4111 * TELEX 06-982311

MICROMEDIA

WE, THE ONTARIO RESEARCH FOUNDATION, STIPULATE THAT THIS DOCUMENT IS SUBJECT TO THE FOLLOWING TERMS AND CONDITIONS:
1. ANY PROPOSAL CONTAINED HEREIN WAS PREPARED FOR THE CONSIDERATION OF THE ADDRESSEE ONLY. ITS CONTENTS MAY NOT BE USED BY NOR DISCLOSED TO ANY OTHER PARTY WITHOUT OUR PRIOR WRITTEN CONSENT.
2. ANY TESTING, INSPECTION OR INVESTIGATION PERFORMED BY US WILL BE CONDUCTED IN ACCORDANCE WITH NORMAL PROFESSIONAL STANDARDS. NEITHER WE NOR OUR EMPLOYEES SHALL BE RESPONSIBLE FOR ANY LOSS OR DAMAGE RESULTING DIRECTLY OR INDIRECTLY FROM ANY DEFAULT, ERROR OR OMISSION.
3. ANY REPORT, PROPOSAL OR QUOTATION PREPARED BY US REFERS ONLY TO THE PARTICULAR MATERIAL, INSTRUMENT OR OTHER SUBJECT REFERRED TO IN IT. NO REPRESENTATION IS MADE THAT SIMILAR ARTICLES WILL BE OF LIKE QUALITY.
4. NO REPORT ISSUED BY US SHALL BE PUBLISHED IN WHOLE OR IN PART WITHOUT OUR PRIOR WRITTEN CONSENT.
5. OUR NAME SHALL NOT BE USED IN ANY WAY IN CONNECTION WITH THE SALE, OFFER OR ADVERTISEMENT OF ANY ARTICLE, PROCESS OR SERVICE.
6. WE RESERVE THE RIGHT NOT TO COMMENCE AND/OR CONTINUE ANY WORK UNTIL PAYMENT ARRANGEMENTS SATISFACTORY TO US ARE ESTABLISHED.

Optimization of Fungal Adsorption of Uranium
for Dept. of Supply and Services

TABLE OF CONTENTS

EXECUTIVE SUMMARY.....1

1. INTRODUCTION.....2

2. EXPERIMENTAL.....2

2.1. Biomass Production.....2

2.2. Sol-Gel Formulation.....3

2.3. Loading and elution tests.....6

2.4. Physical sol-gel biomass characterization.....9

3. RESULTS AND DISCUSSIONS.....9

3.1. Sol Gel Formulation.....9

3.2. Loading and elution tests.....11

3.3. Physical sol-gel biomass characterization.....15

4. CONCLUSIONS.....16

5. RECOMMENDATIONS.....17

6. CONTRACT PLAN, WORK PROGRAM AND CASH FLOW.....18

7. REFERENCES.....19

TABLES.....20

FIGURES.....45

APPENDIX.....65

Biomass Production.....

EXECUTIVE SUMMARY

The objective of this study was to prove repeat loading capacities of physically stabilized fungal biomass from Penicillium sp. for the recovery of uranium from Denison mine water. The testwork was carried out on a bench scale in small columns and proved that it is possible to stabilize the biomass by a sol-gel. This sol-gel is based on the reactants sodium silicate and aluminum chloride. A lifetime of 10 loading - eluting cycles of the sol-gel biomass product was obtained by alternating pretreatment with sodium carbonate, sulphuric acid and ethanol as well as by intermittent wet classification. Sodium carbonate proved to be an effective elution medium. Loading and elution can be controlled by the pH values of the effluents of the column. The effective loading capacity until the break through point is approximately 70% of the overall loading capacity. The loading capacities of the sol-gel biomass product are comparable to that of the original biomass. Uranium recoveries of 90 to 100% were achieved during the loading and eluting under optimal conditions. Further optimization of the loading capacity of the biomass and scale-up work are suggested.

1. INTRODUCTION

The recovery of uranium from Denison minewater by bioadsorption has been successfully studied under DSS contract (14 SQ.23440-6-9042). It was found that a sufficient loading capacity of 150 mg U/g dried biomass was achieved under batch stirred tank conditions. The biomass was obtained from Penicillium sp. at yields of 20-24g dried material per L Medium TM after 48-60 hours. The objective of this study is to prove repeat loading capacities of the physically stabilized biomass on a bench scale.

2. EXPERIMENTAL

The experimental work is divided into four tasks.

Task 1 Production of up to 1,000g biomass

Task 2 Development of a suitable sol-gel formulation for biomass stabilization.

Task 3 Bench scale repeat loading and elution tests at two different flow rates and with two different eluants (NaCl, Na_2CO_3).

Task 4 Physical characterization of the physically stabilized biomass (sol-gel biomass) prior to and after repeated loading and elution cycles.

2.1. Biomass Production

The production of the biomass has been contracted to Mac Master University and the Biotechnological Department of Ontario Research. The foregoing work was completed and 300 g of biomass were obtained. This biomass was a washed and heat treated material (120°C, autoclave, see Appendix).

2.2. Sol-Gel Formulation

Five possible sol-gel formulations were chosen for the test work. They are based on the following reagents:

A) Aluminum tri sec butoxide, tetraethyl-ortho-silicate in ethanol solutions and ammonia water for catalysis and hydration.

B) Sodium silicate and magnesium chloride in aqueous solution and ammonia water for possible catalysis.

C) Sodium silicate and aluminum chloride in aqueous solution and ammonia water for possible catalysis.

D) Sodium silicate and barium chloride in aqueous solutions and ammonia water for possible catalysis.

E) Sodium silicate and barium acetate in aqueous solutions and ammonia water for possible catalysis.

F) Sodium silicate and barium acetate in aqueous solutions and acetic acid for possible catalysis.

The sol-gel preparation tests are based on 10% solutions with a total volume of 200 ml of the reactants. The parameters studied were the relative amounts of reactants and additions of ammonia wate. or acetic acid.

The sol-gels produced are evaluated for their wet porosity, volume change (shrinkage), weight loss on heating at temperatures of 85^{o}C and 200^{o}C plus their resistance to sulphuric acid and sodium carbonate solution. The total dry weight of the sol-gels indicates the weight recovery acheived.

The observed volume changes are reported as linear shrinkage (in %), whereas the resistance to sulphuric acid and sodium carbonate solutions are expressed in mechanical stability and weight losses after leaching tests.

Weight losses on heating and the related wet porosity and volume changes indicate the degree of permeability of the sol-gels. The porosity should be large enough to allow sufficient mass transfer between the pregnant solution and the bio-resin (biomass) through capillary action. A sol-gel of higher porosity with high weight losses on heating and low volume change (shrinkage) would be most desirable.

Resistance of the sol-gel to the loading medium, sulphuric acid, and sodium carbonate solution as the stripping medium is an essential requirement since it influences directly the durability of the sol-gel biomass in ion exchange application. The highest chemical resistance is marked by the lowest losses and best mechanical stability after leaching tests.

The tests to produce the different sol-gels were carried out at room temperature if not otherwise stated and according to the following procedure:

- preparation of a 10% solution of Aluminum trisec butoxide in ethanol or of sodium orthosilicate in water in a beaker with magnetic stirrer (approx. 3-5 min)

- addition of second reactant (Si-, Al-, Mg-, or Ba- compounds) in required amount and mixing for 5 min

- addition of ammonia water or acetic acid and mixing for 5 min

- aging of mixture for 12 hrs with limited air exposure

- filtration of gel and cutting of cylindrical test bodies for determination of wet porosity and linear shrinkage on drying

- drying of samples at 85°C and 200°C and determination of total dry weight (= recovery), weight losses and shrinking

- chemical resistance tests with approx. 0.5 g dry sample material in each -50 ml of H_2SO_4(pH2) and 50 ml of Na_2CO_3 solution (30%) for 12 hrs (without agitation)

- filtration, drying (85°C, 6 hrs) and weighing of leaching residues

- after each drying and filtration step, the mechanical stability of the obtained material was observed

From the above sol-gel formulations type A and C were selected for further tests with biomass. Both sol-gel types, A and C, were applied separately to slurries of biomass by the following procedures:

A: 5 g of Biomass were dispersed in 150 ml solution consisting of 50 ml of 10% Al-trisec butoxide in ethanol and 100 ml of 10% tetraethyl - orthosilicate in ethanol for 5 min. Then 3 ml of 10% ammonia water were added and stirring was continued for 1 min. After filtration for 12 hours and drying at 85°C, 6.9 g of a light sol-gel biomass were obtained.

C: 5 g of Biomass were dispersed in 50 ml of aqueous solution of aluminum chloride (10%) for 5 min. Then 100 ml of distilled water and 50 ml of 10% aqueous solution of sodium silicate were added and stirring was continued for 1 min. After filtration for 12 hours and drying at 85°C, 29.7g of a dense sol-gel biomass were obtained.

Both sol-gel biomass products were comminuted to -2.3 mm and portions of 0.5 g were tested for weight-loss during three stages of alternating acidic and alkaline treatment. The acidic treatment consisted of exposure to sulphuric acid (pH 3) for 12 hours to simulate loading conditions. Elution conditions were simulated by an alkaline treatment for 12 hours using 10% sodium carbonate solution.

2.3. Loading and elution tests

For the loading and elution tests two initial sol-gel biomass types were produced, which were based on sol-gel type C. The procedures were as follows:

type I: 10g Biomass were dispersed in 100 ml aqueous solution of aluminum chloride (2.5%) by stirring for 5 min. Then 50 ml of aqueous sodium silicate solution (5%) and 15 ml ammonia water (10%) were added and stirring was continued for 1 min. After 30 min filtration and drying for 2 hrs at 85°C approximately 11g of sol-gel biomass were recovered per batch.

type II: 10g Biomass were dispersed in 100 ml aqueous solution of sodium silicate (2.5%) by stirring for 5 min. Then 50 ml aqueous aluminum chloride solution (5%) and 15 ml ethanol were added and stirring was continued for 1 min. After 30 min filtration and drying for 2 hrs at 85°C approximately 12g of sol-gel biomass were recovered per batch.

In both cases the sol-gel biomass products were carefully broken to -1.18 mm and the resulting fraction -0.106 mm (=1%) was recycled to the next batch. Overall, 60g of sol-gel biomass were produced in this mode.

The loading elution tests were carried out with 3g of the sol-gel biomass types I and II at different flow rates. Uranium bearing mine water was the loading medium in all cases. The initial mine water did show a pH of 2 and a U-concentration of 49 ppm. Prior to the loading tests the pH of the mine water was adjusted with sodium hydroxide at pH 4.2. This caused a decrease of the U concentration to 41.5 -47 ppm. Sodium chloride and sodium carbonate were used as eluants. The laboratory set-up consisted of glass columns of 1.1 cm in diameter, giving an approximate height of 10 cm and a volume of 10 ml of the sol-gel biomass ion exchange bed. The feedrate was controlled with a peristaltic pump and the column effluents by gravity.

For control purposes, an agitated batch loading test was conducted with 1g pure biomass in 1L of pH 4 mine water. The loading time was 3 hrs.

After four initial loading and elution column tests the composition of the elution media and the flowrate were changed during 5 subsequent tests, to avoid column plugging and to possibly increase the uranium recovery from the solution.

A further modification of the sol-gel biomass was necessary prior to a final 10 cycle loading elution test. The objective of this modification was to chemically stabilize the sol-gel biomass by alternating alkaline and acidic pretreatment, to pre-conditions the biomass with alcohol and to come to a coarser size fraction which is less sensitive to swelling during elution. The modified procedure was as follows:

- 7g of sol-gel biomass type II were treated in a stirred beaker with 150 ml of 10% sodium carbonate solution, then filtered and washed with 100 ml distilled water.

- The remaining solids were washed with 100 ml of pH 3 sulphuric acid and subsequently treated with 10 ml of 10% sodium carbonate solutions, followed by intense washing with distilled water and 2 x 30 ml ethanol.

- After drying for 1 hr at 85°C, the sol-gel biomass was carefully comminuted to -1.18 mm and the size fraction -0.3 mm was removed.

- To prevent the extraction column from further plugging, it was necessary to remove the size fraction -0.425 mm after the first loading elution cycle of the test.

The weight losses were 44% after the chemical treatment, 56.4% after removing the fraction -0.3mm and 69% after the removal of the fraction -0.425mm. The resulting column loads with sol-gel biomass were 3.05g during the first loading elution cycle and 2.17g during the loading elution cycles 2 to 10. After removing the fraction -0.425 mm the heights of the column load remained constant at 10 cm, because the particles of this fraction filled the free spaces between the coarser sol-gel biomass grains. The sol-gel biomass product described is referred to as sol-gel biomass type III. The final loading elution test consisted of 10 loading elution cycles. A flowrate of approx. 40 BV/hr (0.4 L/hr) was chosen for the loading as well as the elution stage. A 5% solution of sodium carbonate was applied as elution medium.

The throughput during the single tests varied between 200 BV (BV = bed volume) and 50 BV during the loading stage and 50 BV and 8 BV during the eluting stage. The basis for evaluation of the tests consisted of the volumes and flowrates of the column effluents as well as their uranium and iron concentrations and pH values. The loading elution capacities were derived from the actual sol-gel biomass weights, the flowrates and uranium concentration differences between the mine water and the loading effluents as well as from the volumes and uranium contents of the elution effluents.

2.4. Physical sol-gel biomass characterization

Prior to and after loading elution tests the three studied sol-gel biomass types studied were analysed for their particle size distributions. These screening analyses should indicate changes due to decomposition of the sol-gel biomass. Furthermore the BET surface area of sol-gel biomass type III was measured before and after the final 10 cycle test.

3. RESULTS AND DISCUSSION

3.1. Sol-Gel Formulation

The evaluation results of the sol-gel formulation A are evaluated and presented in Table 1 and Figs. 1,2 and 8. The dry weights of the gels produced are low when compared to the theoretical maximum of 20g. The weight losses on heating, the observed shrinkages and measured wet porosities indicate the gels may be suitable for biomass inclusion. The weight losses measured after sulphuric acid treatment are again encouraging. After treatment with sodium carbonate solution weight gains were observed in most cases. Besides the influence of the ratio of the main additives (Al-trisec-butoxide and tetraethyl orthosilicate) additions of more than 15% H_2O and 0.75% NH_4OH seem to be detrimental to the mechanical stability of the gels and cause an unstable behaviour during alkaline treatment with Na_2CO_3. Based on the total dry weight of the sol-gel produced and the associated leaching behaviour, the sol-gel formulation of 1 part Al-trisec-butoxide and 2 parts tetramethyl orthosilicate with an addition of 1% H_2O and 0.1% NH_4OH is regarded as the most promising.

Table 2 and Figs 3 to 7 and 9 to 13 show the results for the formulations C to F which are based on aqueous solutions. In comparison to Formulation A (Table 1) all formulations documented in Table 2 show a higher yield (total dry weight) and higher weight losses on heating as well as increased porosities. However, the measured shrinkage and the weight losses measured after leaching are considerably higher.

Formulation B produces sol-gels of good mechanical stability at high total dry weights and porosities, but parallel to this the shrinkage and weight losses on leaching are also increased.

Sol-gels from formulation C show lower total dry weights (recoveries) but improved mechanical stability and resistance during the leaching tests. Their wet porosity and weight losses on heating are similar to sol-gels of type B.

The sol-gels from the formulations D to F are based on barium compounds. In spite of extended optimization test series (TSG 14 to 24) no distinct improvements of their mechanical stability were made. The total dry weights, weight losses on heating and wet porosities are comparable to the gel types B and C, whereas the shrinkage and weight losses on leaching improved on the tests T-SG-23 to T-SG-26.

Table 3 summarizes the most promising test results for the different sol-gel formulations. The highest mechanical stability and the lowest leaching weight losses were observed for the sol-gel types A and C. Their recovery (of total dry weight) is relatively low, while an increased stability of initial wet pore volume is expected to be high for gel type A and average for type C. Even though the weight recovery of the sol-gel types B, D and E are substantially higher, they show insufficient weight losses on leaching and decreased mechanical stabilities. In spite of a modestly improved mechanical stability the sol-gel type F gave unsatisfactory results.

Following the results shown in Table 3, the most promising sol-gel formulation types A and C were chosen for further tests with biomass. Both sol-gel types were applied separately to slurries of biomass (procedure see 3.2.).

The resulting sol-gel biomass type A was soily, dark brown and tended to float on aqueous solutions and water. The sol-gel biomass type C was very hard, light brown and did not float on aqueous solutions. A yellowish colour and an oily fraction of the filtrates during sol-gel formulation indicated a partial decomposition of the biomass .

Table 4 shows the cumulative weight losses of the sol-gel biomass products during different orders of the treatment stages. The cumulative weight losses of sol-gel biomass type A were up to 36.9% after 3 stages and the rates of increase of weight loss indicate a life time of less than 11 stages. In contrast to that, the maximum weight loss of the sol-gel biomass type C was 31.9% after 3 stages and the rate, at which the weight losses increased, was very low after the second stage. This points out that a significant higher lifetime can be expected for sol-gel biomass type C when compared with sol-gel biomass type A. Additionally, intense swelling of sol-gel biomass A material was observed during alkaline treatment.

3.2. Loading and Elution Tests

The stirred batch loading test with pure biomass, which was carried out for control purposes, gave the following result:

The remaining U concentration of 39 ppm in solution leads to a loading capacity of 5-10 mg U per g of biomass. This relatively low loading capacity may be explained by the initially low U- concentration of approx. 43 ppm in the loading medium as well as by an alteration of the biomass in the production stage (see Appendix). Previous testwork with higher U - concentrations could establish loading capacities of up to 150 mg U per g biomass.

Further to the results of 3.1. the loading and elution tests were conducted with a sol-gel biomass, which was based on sol-gel type C.

Two sol-gel biomass mixtures were initially tested. Sol-gel biomass II represents a lighter, porous material, whereas the sol-gel biomass I is of higher stability. The sol-gel biomass production is described in 2.2.

The results for a series of four tests conducted at a flowrate of 70 BV/hr (0.7 L/hr) are shown in the Tables 5 to 8 and Fig. 14. The loading data establish a significantly higher loading capacity of sol-gel biomass type II of up to 6.1 mgU/g sol-gel biomass, which is compatible to that of the pure biomass. However, the flowrate appeared to be too high causing a mean of 18 ppm U in the effluent waters from the first sampling period. With a maximum of 4 ppm in the resulting effluents, sodium chloride proved to be less effective as elutant. Sodium carbonate as elutant gave 100% U recovery, but it triggered also intensive swelling of both sol-gel biomass types. This swelling caused plugging of the columns, which prohibited further loading elution cycles. As expected from earlier results, the weight losses of the sol-gel biomass after the loading elution tests were higher after elution with sodium carbonate and especially increased with sol-gel biomass type II.

To overcome the problems of plugging or inefficient elution, three loading elution tests were conducted with sol-gel biomass type I and aqueous solutions with 20% of different mixtures of sodium chloride and sodium carbonate as elution media. The average effluent flowrate during elution was measured to monitor the plugging effects. The average pH of the elution effluents as well as the weight losses of the sol-gel biomass were determined for further process control. The results of these tests are given in Table 9. As the ratios of sodium chloride to sodium carbonate increase the plugging effects decrease, which is indicated by higher flowrates. The effluent's pH and weight loss of the sol-gel biomass decrease in parallel. These observations lead to the conclusion, that besides volume increases the reason for plugging might be the partial

dissolution and reprecipitation of the sol-gel biomass. For the anticipated minimal elution medium flowrate of 35 BV/hr (0.35 L/hr) a ratio of 2900 parts sodium chloride to 1 part sodium carbonate in the solution medium was determined by extrapolation. This is approx. equal to a sodium carbonate concentration of 0.007 % and would result in an elution effluent pH value of 8.0.

To achieve increased uranium recoveries and avoid column plugging a loading elution test was carried out with sol-gel biomass type II at a lower loading flowrate of 47 BV/hr (0.47 L/hr) and with a pH 9.2 sodium carbonate solution. The results are shown in Table 10 and Figure 15. The lower loading flowrate caused a further decrease of the U concentration in the initial loading effluents, but a very low overall loading capacity was determined. No plugging was observed during elution. However, low pH values and U concentrations in the elution effluents showed that the diluted sodium carbonate solution is an ineffective elution medium. Replacing the initial elution medium by a sodium carbonate solution with pH 10 did not improve the result. The very low pH values of the elution effluents indicate that sulphuric acid was also adsorbed during the loading stage.

The results of the final loading elution test (test 9/10 cycles/sol-gel biomass type II) are documented in Tables 11a to 11k and Figures 16 to 19.

During the first minutes of the loading cycles very high extraction rates were observed. Depending on the amount of sol-gel biomass in the column (3.05 g in cycle 1, initially 2.17 g in cycles 2 to 10) the break through point varies between 15 BV (150 ml) and 25 BV (250 ml) of mine water. For a given throughput of 500 ml minewater (50 BV) the overall loading elution capacity varies between 4 and 6 mg U/g solids of sol-gel biomass without showing a negative trend (Fig 17). It increases up to approx. 7 mg U/g

sol-gel biomass, which is higher than the loading capacity of the pure biomass (stirred batch test), provided a content of approximately 50% biomass in the sol-gel biomass product. Based on a breakthrough point at 15 BV (150 ml) mine water throughput (ion exchange bed heights 10 cm, bed volume 10 cm^3), the average effective loading capacity is 3 mg U/g sol-gel biomass.

A total of 8 BV (80 ml) elution medium and an elution time of 12 to 14 min proved to be sufficient for the chosen test conditions (Fig 18). The resulting average enrichment causes U concentrations in the elution effluents, which are 3 to 4 times higher than those in the loading media. These enrichment factors could be increased to minimal 10 by lowering the throughput of the elution medium.

The ion exchange reactions during loading as well as eluting are controlled by the pH value. It is therefore possible to monitor the process stages by measuring the pH values in the column's effluents. Figure 20 shows that a pH of 5 indicates the break through point during loading, while pH values of 11 to 11.5 are typical for the end of successfull elution.

It might be concluded from the yellowish colour of the elution effluents that Fe^{3+} ions are adsorbed by the biomass together with uranium, which could affect the loading capacity. Another negative affect would be the partial dissolution of the biomass as starch like composite. Analyses of the iron content in the minewater and the column effluent prove that iron is absorbed and desorbed parallel with uranium, but its low concentrations do not hamper the uranium loading elution capacity of the biomass. Partial dissolution of the biomass however, is indicated by weight losses of the sol-gel biomass of approximately 5% per stage.

Whereas the loading elution capacity of the sol-gel biomass remained relatively stable (Fig 17), difficulties were encountered due to fine flaky precipitation. These precipitates are derived from dissolved sol-gel biomass during elution as well as from the SiO_2 content of the mine water during the early time intervals of the loading stages. After the nineth loading elution cycle it became necessary to remove the precipitates by wet screening at 0.3 mm, to avoid plugging of the column. The weight distribution of the discarded fine fraction was 46.1%.

3.3. Physical Sol-Gel Biomass Characterization

The sol-gel biomass types I, II, and III were analysed for their particle size distributions prior to and after loading elution tests. The results are given in Tables 12a to c. The presence of fines in the original material causes extensive caking of the final products. This finds its expression in a pronounced increase of the particle size fraction +0.84 mm after the column tests. The still relatively high weight distribution of approximately 20% in the fraction -0.425 mm of the final products might be due to reprecipitation. Less pronounced changes in the partical size distribution of sol-gel biomass type III give evidence of the effectiveness of the measures (pretreatment, intermittent sizing) to avoid reprecipitated fines.

BET analyses of sol-gel biomass type III show an increase of the surface area from initially 0.44 m^2/g to 6.4 m^2/g after the last loading cycle of test 9. This can be explained by a higher porosity due to leaching effects. The slight tendency towards improved loading elution capacities with increased loading elution cycle numbers might be caused by this phenomenon.

4. CONCLUSIONS

The testwork undertaken proves that it is possible to physically stabilize a biomass for uranium extraction in ion exchange columns by a sol-gel. This sol-gel is based on the reactants sodium silicate and aluminum chloride and can easily be formed in aqueous solutions. To improve the properties (porosity and surface area) of the sol-gel as well as of the biomass, the sol-gel biomass formulation should be enhanced by the addition of ethanol during its formation. A life time of the sol-gel biomass of more than 10 loading elution cycles without plugging or extensive decomposing can be achieved by the following measures:

1) Alternating pretreatment (washing) with sodium carbonate solution, sulphuric acid and ethanol.

2) Restricting the lowest size of the sol-gel biomass particles to the range between 0.6 and 1.0 mm.

3) Alternating flowdirections for the different loading, washing and eluting stages, which might be accompanied by fluidizing the ion exchange bed in a washing stage after each 5th cycle to remove fine precipitates.

4) Limiting the exposure to the elution medium to the lowest possible amount.

Losses of biomass during sol-gel biomass preparation and in intensified (fluidizing) washing cycles might be minimized by recycling the recovered fine particle fractions into the sol-gel biomass production stage. The possible recovery by this measure could be more than 50%.

Repeat loading elution cycle testing established that under the given test conditions the effective loading capacity until the break through point

is approximately 60-70% of the overall loading capacity. Out of the two elution media tested, sodium carbonate and sodium chloride, only sodium carbonate is effective. This can be explained by the fact that only sodium carbonate provides a pH value above 11, which appears to be necessary for successful elution. The loading elution process can be monitored via the pH values in the columns effluents: A pH of 11 to 11.6 marks the end of elution, whereas a pH value of 5 indicates the break through point during loading. Using the effective loading capacity, uranium recoveries of 90 to 100% were achieved in the loading and elution stages.

The loading elution capacity of the sol-gel biomass corresponds with the original biomass (as received). The overall loading capacity of the original biomass was established at 5 to 10 mg uranium per g biomass, which is low when compared to 150 mg/g in earlier studies. The reason for this is very likely, that the biomass batch as received was not identical to the previously tested material and that the U content of the Minewater was three times lower than in the earlier tests.

5. RECOMMENDATIONS

From the results obtained further development work is suggested as follows:

- Optimization of biomass production in order to maintain a constantly high loading capacity of the biomass.

- Repeat loading elution column tests with varying particle sizes of the sol-gel biomass load to minimize sol-gel biomass losses.

- Repeat loading elution column tests with recycling of fine sol-gel biomass rejects into the sol-gel biomass production stage.

- Scale up testwork using three different column sizes and ion exchange bed heights.

6. CONTRACT PLAN, WORK PROGRAM AND CASH FLOW

The additional work, which was necessary to optimize the loading elution test conditions and equalize delays in biomass production, caused a shift of the expenses towards task 3.0 (Loading/Elution) and an extended time plan. This is documented in Table 13. In spite of the changes mentioned the project's tasks were completed in accordance to the overall financial and contract planning.

V.I. Lakshmanan
Project Manager
Mineral Resources

G. Heinrich
Project Scientist
Mineral Resources

for G.M. Freeman
Operations Manager
Mineral Resources

REFERENCES:

1) DSS File No 15 SQ23440-5-9181: 'Comparison of Bioadsorption Capacity of Denison Mine Isolates with Organisms Previously Assessed; 'Final Report (July 1986).

2) Lakshmanan, V.I., Christison, I., King, D.J., Trezos, M., & McCreedy, R.G.L. 'Optimization of Fungal Adsorption of Uranium and Cell Immobilization'; Presentation at Annual Biominet Meeting, Sudbury (Nov. 1987).

3) Dislich, H: 'Glassy and Crystalline Systems from Gels: Chemical Basis and Technical Application'; Journal of Non-Crystalline Solids 57 (1987) p. 371-388.

4) Klein, L.C.: 'Sol Gel Glass Technology Updata'; The Glass Industry (May 1982) p. 27-29.

5) Carturan, G., Gottardi, V, & Graziani, M: 'Physical and Chemical Evolution Occuring in Glass Formulation from Alokoxides of Silicon, Aluminum and Sodium'; Journal of Non-Crystalline Solids 29 (1978) p.41-48.

6) Brinker, C.J., & Mukherjee, S.P.: 'Conversion of Monolithic Gels to Glasses in a Multicomponent Silicate Glass System'; Journal of Materials Science 16 (1981) p.1980-1988.

7) Hayashi, T., & Saito, H.: 'Preparation of Ca O - SiO_2 Glasses by the Gel Method'; Journal of Materials Science 15 (1980) p.1971-1977.

TABLES

Table 1

Evaluation of Sol-Gel types (formed from 10% solutions)
Formulation A

Test #	Constituents total of a+b = 200 ml	Total dry weight (g)	Weight loss in % at 85°C	Weight loss in % at 200°C	Length & width Shrinkage in %	Wet Porosity (vol %)	Mechanical Stability initial	Wt. loss with Acid in %	Wt. loss with Alkaline in %	Mechanical Stability after leaching
T-SG-1	1a:1b -0.02 c	3.05						-18.1	+13.4	+
T-SG-2	2a:1b -0.02 c	3.54						-15.5	+1.2	-
T-SG-3	1a:2b -0.02 c	4.29						-16.6	+5.4	++
T-SG-4	1a:1b -0.03 d	2.9	81.0	81.1	17.4	60.2	+	-2.1	+52.5	o
T-SG-5	2a:1b -0.03 d	3.43	85.1	86.4	21.6	72.2	+	+2.3	+101.4	o
T-SG-6	1a:2b -0.03 d	2.29	76.4	80.6	18.2	50.9	+	-2.6	+32.6	-
T-SG-7	1a:1b -0.15 c	4.1	87.0	89.6	36.4	81.6	-	-8.4	+73.0	o
T-SG-28	200 mla + 50 mle 0.05 c	4.27	83.9	83.5	17.1	78.3	- -	-2.0	-42.3	- -

Legend

Constituents used

a - 10 % Aluminum tri-sec butoxide - ethyl alcohol denatured
b - 10 % Tetraethyl orthosilicate - " " "
c - 10 % NH_4OH - distill H_2O
d - 1 % NH_4OH - distill H_2O
e - 10 % Barium Acetate - distill H_2O

Mechanical Stability (when wet)

+ hard
- soft

Table 2

Evaluation of Sol-Gel types (formed from 10% solutions)
Formulation B CT-SG 8, 9, 10
C CT-SG 11, 12, 13
D CT-SG 14, 15, 16
E CT-SG 17, 18, 19
F CT-SG 20, 21, 22, 25, 26/23, 24

Test #	Constituents total of a+b = 200 ml a+c = 200 ml a+d = 200 ml a+e = 200 ml	Total dry weight (g)	Weight loss in % at 85°C	Weight loss in % at 200°C	Length & width Shrinkage in %	Wet Porosity (vol %)	Mechanical Stability initial	Wt. loss with Acid in %	Wt. loss with Alkaline in %	Mechanical Stability after leaching
T-SG-8	1a:1b -0.15 f	6.98	90.2	90.6	61.0	89.4	++	-39.5	-9.0	+
T-SG-9	2a:1b -0.15 f	7.75	91.0	90.0	53.2	94.2	+	-31.6	-16.5	+
T-SG-10	1a:2b -0.15 f	6.27	90.0	90.2	61.8	92.1	++	-41.3	-21.1	+
T-SG-11	1a:1c -0.15 f	4.67	95.3	94.4	63.3	84.5	+	-23.3	+8.8	++
T-SG-12	2a:1c -0.15 f	5.13	89.1	91.6	63.6	94.7	glassy	-30.5	-13.8	++
T-SG-13	1a:2c -0.15 f	3.96	95.6	95.5	70.4	86.7	++	-22.9	-11.3	++
T-SG-14	1a:1d -0.15 f	8.19	90.0	88.3	45.3	—	-	+5.9	-49.2	- -
T-SG-15	2a:1d -0.15 f	9.14	90.7	89.4	54.2	86.1	-	+1.7	-73.2	- -
T-SG-16	1a:2d -0.15 f	7.85	89.1	87.5	51.5	93.1	-	-12.2	-54.9	- -
T-SG-17	1a:2e -0.15 f	7.89	87.8	86.4	54.5	94.7	-	+0.3	-46.8	- -
T-SG-18	1a:4e -0.15 f	6.4	86.1	85.8	54.5	84.6	-	-15.1	-51.8	+
T-SG-19	1a:8e -0.15 f	3.93	83.2	85.2	45.6	96.8	0	-10.3	-47.4	- -
T-SG-20	1a:2e -0.15 g	6.24	87.0	87.9	54.4	83.7	-	-10.5	-57.3	+
T-SG-21	1a:4e -0.15 g	4.37	86.2	87.4	55.6	95.3	-	-12.9	-43.3	+
T-SG-22	1a:8e -0.15 g	2.36	83.6	85.6	39.4	—	- -	-9.7	-80.9	-
T-SG-23	2a:1d -0.15 g	7.52	89.7	89.3	48.1	90.9	-	-0.5	-23.3	o
T-SG-24	4a:1d -0.15 g	8.07	89.6	88.8	43.6	93.9	-	-10.4	-23.4	o
T-SG-25	2a:1e -0.15 g	7.65	89.8	88.2	49.0	86.2	- -	-3.8	-11.8	o
T-SG-26	4a:1e -0.15 g	7.07	90.0	88.4	42.3	95.3	- -	-9.3	-37.9	o

Legend

Constituents used

a 10 % Sodium Silicate - distill H_2O
b 10 % $MgCl_2$ - " "
c 10 % $AlCl_3$ - " "
d 10 % Barium Chloride - " "
e 10 % Barium Acetate - " "
f 10 % NH_4OH - " "
g 10 % Acetic Acid - " "

Mechanical Stability (when wet)

+ hard
- soft
o neutral

TABLE 3

Summary of most promising tests per sol-gel type, comparison of critical evaluation parameters.

Formulation	Test No.	Mechanical stability after leaching (+, o, -)	Average leaching wt-loss (%)	Total dry weight (yield) (g)	Moisture (200°C) shrinkage (%/%) *)
A	T-SG-3	++	-5.6	4.29	--
A	T-SG-4	o	+25.2	2.9	4.66
B	T-SG-9	+	-24.1	7.75	1.69
C	T-SG-11	++	-7.25	4.67	1.49
D	T-SG-14	--	-21.7	8.19	1.95
E	T-SG-18	+	-33.5	6.40	1.57
F	T-SG-21	+	-28.1	4.37	1.57

*) higher values indicate increased stability of pore volumina.

TABLE 4

Cumulative weight losses of sol-gel biomass type A and C during 3 stages of acidic and alkaline treatment

treatment stage	treatment/ result	Sol-gel biomass A		Sol-gel biomass C	
1	condition	acidic	alkaline	acidic	alkaline
	wt. loss (%)	12.6	15.3	25.2	22.3
2	condition	alkaline	acidic	alkaline	acidic
	wt. loss(%)	18.4	34.1	28.8	30.6
3	condition	acidic	alkaline	acidic	alkaline
	wt. loss(%)	33.5	36.9	31.9	31.2

TABLE 5

Results for loading elution test 1 (conditions: biomass from production without ethanol, type I, flowrate 0.7L/hr, elution with 10% Na Cl - solution, after 3X washing).

mode	time(min)	effluents: Volume (ml)	U-conc. (ppm)	U-content (mg)	(%)	comments
loading	0-30	359	18	8.8	57.6	3.5 mg U/g
	30-60	365	39	1.3	8.2	loading
	60-90	375	42	0	0	capacity
	90-120	360	43	0	0	
	120-150	365	42	0	0	
	150-165	172	43	0	0	
washing	0-2	21	33	0.7		
	2-4	21	11	0.2		
	4-6	21	7.2	0.15		
eluting	0-11	120	2.8	0.34	3.4	7.5%
	11-22	128	1.3	0.17	1.7	recovered
	22-33	128	1.1	0.14	1.4	in
	33-44	130	0.8	0.10	1.0	solution
washing	0-2	21	1.4	0.03		wt loss
	2-4	21	4.0	0.08		of solids
	4-6	21	8.6	0.18		3.7%

TABLE 6

Results for loading elution test 2 (conditions: biomass from production with ethanol, type II, flowrate 0.7L/hr, elution with 10% Na Cl - solution, after 3X washing).

mode	time(min)	effluents: Volume (ml)	U-conc. (ppm)	U-content (mg)	(%)	comments
loading	0-30	424	9.9	13.8	76.7	6.1 mg U/g
	30-60	375	38	1.7	10.6	solids
	60-90	415	41	0	0	loading
	90-120	265	44	0	0	capacity
	120-150	320	41	0	0	
	150-175	245	44	0	0	
washing	0-2	20	37	0.74		
	2-4	21	15	0.32		
	4-6	21	11	0.23		
eluting	0-11	128	4.1	0.52	3.4	6.4%
	11-22	130	1.8	0.23	1.5	recovered
	22-33	126	1.0	0.13	0.8	in
	33-45	120	0.9	0.11	0.7	solution
washing	0-2	20	0.9	0.018		
	2-4	20	5.7	0.114		wt. loss
	4-6	21	12.0	0.252		of solids
						14.7%

TABLE 7

Results for loading elution test 3 (conditions: biomass from production without ethanol, type I, flowrate 0.7L/hr, elution with 10% Na_2CO_3 - solution, after 3X washing).

mode	time(min)	effluents: Volume (ml)	U-conc. (ppm)	U-content (mg)	(%)	comments
loading	0-30	394	21	7.1	46.2	3.5 mg U/g
	30-60	395	34	2.0	12.8	solids
	60-90	314	43	0	0	loading
	90-120	288	35	0	0	capacity
	120-150	295	35	0	0	
	150-181	330	43	0	0	
washing	0-2	20	29	0.58		
	2-4	20	16	0.32		
	4-6	20	7.2	0.14		
eluting	0-71	38				100%
	71-86	2	140	9.24		recovered
	86-146	26				in solution
						(colour:
						yellow) wt.
						loss of
						solids
						13.7%

TABLE 8

Results for loading elution test 4 (conditions: biomass from production without ethanol, type II, flowrate 0.7L/hr, elution with 10% Na_2CO_3 - solution, after 3X washing).

mode	time(min)	effluents: Volume (ml)	U-conc. (ppm)	U-content (mg)	(%)	comments
loading	0-30	392	24	7.2	43.2	4.3 mg U/g
	30-60	397	40	0.9	5.3	solids
	60-90	380	40	0.9	5.3	loading
	90-120	388	42	0.2	1.2	capacity
	120-150	398	43	0	0	
	150-156	75	44	0	0	
washing	0-2	20	39	0.78		
	2-4	21	13	0.27		
	4-6	21	10	0.21		
eluting	0-10	37	192	7.1	77.2	100%
	10-795	71	30	2.1	22.8	recovered in solution (cloudy, yellow) wt. loss of solids 29%

TABLE 9

Influence of the ratio of the NaCl to Na_2CO_3 in 20% solutions on the average effluent flowrate during elution and other parameters (loading - elution tests 5 to 7, sol-gel biomass type I).

ratio NaCl:Na_2CO_3	effluent flowrate (L/hr)	effluent pH	weight loss of sol-gel biomass (%)
1:1	0.016	10.8	11.7
2:1	0.020	10.5	8.3
10:1	0.039	9.9	8.0
2900:1 (=0.007% Na_2CO_3)	0.35 *)	8.0 *)	

*) extrapolated

TABLE 10

Results for loading elution test 8 (conditions: sol-gel biomass type II, flowrate 0.47L/hr, elution with pH 9.2 Na_2CO_3 solution after 3X washing).

mode	time(min)	Volume ml	pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-12	98	4.36	7.4	3.3	82.2	2.0 mg U/g
	12-24	98		23	1.8	44.6	solids
	24-36	98		34	0.7	18.1	loading
	36-45	58		37	0.3	10.8	capacity
washing	0-6	58		5.4	0.3		
eluting	0-4	29	3.53	2.9	0.08	1.3	3.0% recovered
	4-8	29		2.0	0.06	1.0	in solution
	8-12	26		1.0	0.03	0.5	
	12-15	15	3.85	0.6	0.01	0.2	
washing	0-6	59	3.53	0.5	0.03		15.3% wt. loss of solids

TABLE 11a

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 1:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-14	106	7.4	0.2	4.4	99.5	
	14-28	104	5.4	0.7	4.2	98.3	4.9 mg U/g
	28-42	100	4.8	10.	3.2	75.9	solids
	42-56	101	4.6	24	1.8	42.2	loading
	56-68	90	4.5	28	1.2	32.5	capacity
washing	0-6	59	4.4	16	0.94		
eluting	0-7	32	10.6	400	12.8	86.5	94.9% recovered
	7-14	34	11.4	35	1.2	8.1	in solution
	21-29	49	11.8	0.6	0.03	0.2	
washing	0-6	58	12.0	<0.1			

TABLE 11b

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 2:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-14	104	5.0	<0.1	4.3	100	5.2 mg U/g
	14-28	96	4.6	13	2.7	68.7	solids
	28-42	98	4.5	22	1.9	47.0	loading
	42-56	94	4.5	31	1.0	25.3	capacity
	56-69	109	4.5	29	1.4	30.1	
washing	0-6	60	4.2				
eluting	0-7	42	11.0	206	8.7	77.0	79.7% recovered
	7-14	43	11.6	7.5	0.3	2.7	in solution
	14-21	44	11.7	<0.1			
	21-24	24	11.8	<0.1			
washing	0-6	57	11.7				

TABLE 11c

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 3:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-14	84	9.5	<0.1	3.5	100	5.1 mg U/g
	14-28	84	5.1	3.6	3.2	91.3	solids
	28-45	102	4.8	20	2.2	51.8	loading
	45-56	56	4.7	30	0.6	27.7	capacity *)
	56-70	82	4.6	31	0.9	25.3	
	70-85	97	4.5	38	0.3	8.4	
washing	0-6	58	4.5				
eluting	0-7	31	10.9	316	9.8	91.6	100% recovered
	7-14	36	11.7	24	0.9	8.4	in solution
	14-21	36	11.9	<0.1			
	21-28	43	11.9	<0.1			
washing	0-6	56	11.9				

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11d

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 4:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-27	166	5.7	<0.1	6.9	100	loading
	27-52	146	4.6	20	3.1	51.8	capacity
	52-78	136	4.5	33	1.2	20.5	(mg U/g solids)
	78-104	142	4.5	36	0.8	13.3	6.7 for 750 ml
	104-129	158	4.5	33	1.3	20.5	5.8 for 450 ml
washing	0-6	60	4.5				*)
eluting	0-7	38	10.7	241	9.2	69.2	73.7% recovered
	7-14	47	11.4	13	0.6	4.5	in solution
	14-21	38	11.5	<0.1			
	21-24	28	11.5	<0.1			
washing	0-6	56	11.7				

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11e

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 5:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-87	500	4.5	(38)	(1.8)		
washing	0-6	60	4.5				
eluting	0-13	80	11.0	129	10.32		5.6 mg U/g solid loading/ elution
washing	0-6	58	11.6				*) capacity

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11f

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 6:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-79	500	4.6	25	8.3	39.8	
washing	0-6	60	4.5				4.6 mg U/g solids loading elution capacity *)
eluting	0-11	80	11.0	98	7.8	100	
washing	0-6	58	11.6				

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11g

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 7:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-29	204	5.0	5.6	7.3	86.5	
	29-58	204	4.5	38	0.7	8.4	
	58-72	89	4.4	45	0	0	5.5 mg U/g
washing	0-6	58	6.6				solids loading
eluting	0-5	22	10.6	377	8.3		elution
	5-10	23	11.1	72	1.7	100	capacity
	10-20	64	11.5	6.0	0.4		*)
washing	0-6	56	11.7				

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11h

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 8:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-72	500	4.54	20	10.8	51.8	
washing	0-6	54	4.48				6.9 mg U/g solids loading
eluting	0-16	80	11.02	130	10.4	96.3	capacity *)
washing	0-6	58	11.64				

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11i

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 9:

mode	time(min)	Volume ml	effluent pH	U-conc. (ppm)	U-extraction (mg)	(%)	comments
loading	0-69	500	4.7	22	9.75	47.0	
washing	0-6	60	4.5				6.5 mg U/g solids loading
eluting	0-49	75	11.0	120	9.0	92.3	elution capacity
washing	0-6	20	11.4				*)

*) based on linear weight loss of 0.104 g sol-gel biomass per cycle

TABLE 11k

Results for loading elution test 9 (conditions: sol-gel biomass type III, 10 loading-elution cycles, flowrate 0.4 L/hr, elution with 5% Na_2CO_3 solution).

Cycle 10:

mode	time(min)	Volume ml	effluent pH	Fe conc. (ppm)	U-conc. (ppm)	U-extraction (mg)	U-extraction (%)	comments
loading	0-43	259	5.0	<0.2	20	5.6	51.8	
	43-78	240	4.5	0.23	38	0.8	8.4	
washing	0-6	60	4.5					5.9 mg U/g solids
eluting	0-7	40	11.0	1.6	141	5.6	87.5	loading
	7-12	41	11.5	<0.2	5.8	0.2	3.1	elution
washing	0-6	56	11.5					capacity

Control analysis of mine water: 44 ppm U
0.41 ppm Fe
pH 4.22

TABLE 12a

Screen analysis of sol-gel biomass type I before and after loading - elution testwork (elution at pH 9)

particle size (mm)	initial material wt. - distribution (%)	sum(%)	material after column test wt. - distribution (%)	sum(%)
+0.84	28.4	100.0	61.5	100.0
0.84-0.6	25.5	71.6	11.5	38.5
0.6-0.425	14.4	46.1	3.9	27.0
-0.425	31.7	31.7	23.1	23.1

TABLE 12b

Screen analysis of sol-gel biomass type II before and after loading - elution testwork (elution at pH 9)

particle size (mm)	initial material wt. - distribution (%)	sum(%)	material after column test wt. - distribution (%)	sum(%)
+0.84	23.5	100.0	57.1	100.0
0.84-0.6	23.5	76.5	16.3	42.9
0.6-0.425	15.5	53.0	8.2	26.6
-0.425	37.5	37.5	18.4	18.4

TABLE 12c

Screen analysis of sol-gel biomass type III before and after loading - elution testwork (elution at pH 9)

particle size (mm)	initial material wt. - distribution (%)	sum(%)	material after column test wt. - distribution (%)	sum(%)
+0.84	41.5	100.0	63.2	100.0
0.84-0.6	26.4	58.5	18.8	36.8
0.6-0.425	15.5	32.1	9.4	18.0
-0.425	16.6	16.6	8.6	8.6

Supply and Services Canada / Approvisionnements et Services Canada

TABLE 13

CONTRACT PLAN AND REPORT FORM – FORMULE DE PROJET DE CONTRAT ET DE RAPPORT

CONTRACT TITLE – TITRE DU CONTRAT: OPTIMISATION OF FUNGAL ADSORPTION OF U

CONTRACTOR – ENTREPRENEUR: ONTARIO RESEARCH FOUNDATION

TASK DESCRIPTION / DESCRIPTION DE LA TÂCHE	TASK DURATION IN MONTHS – DURÉE DE LA TÂCHE EN							
	1 FEB	2 MAR	3 APRIL	4 MAY	5	6	7	8
1.0 Biomass Production								
2.0 Sol-Gel Formulation								
3.0 Loading/Elution								
4.0 Final Biomass Evaluation								
PLANNED COST BY MONTH / COÛT PRÉVU POUR CHAQUE MOIS	3682	9012	9012	9012				
ACT. PRÉCÉD. / E.T.C. BY MONTH / PRÉVISION POUR CH. MOIS	2769	8796	8539	11,796				

BLE 13

DSS-MAS 0143-3 (4/8

RAT ET DE RAPPORT

ION OF FUNGAL ADSORPTION OF URANIUM
ARIO RESEARCH FOUNDATION

FILE NO. - N° DU DOSSIER

SERIAL NO. - N° DE SÉRIE
23440-7-922/01-SQ

DURATION IN MONTHS - DURÉE DE LA TÂCHE EN MOIS

TASK COST - COÛT DE LA TÂCHE

6	7	8	9	10	11	12	PLANNED PRÉVU À L'ÉTUDE	ACTUAL DÉPENSES À CE JOUR	E.T.C. À VENIR
							4,500	4,000	
							10,000	10,000	
							7,000	12,000	
							9,400	4,900	
							PLAN 30,900		
								ACTUAL COÛTS RÉELS 30,900	E.T.C. À VENIR

FIGURES

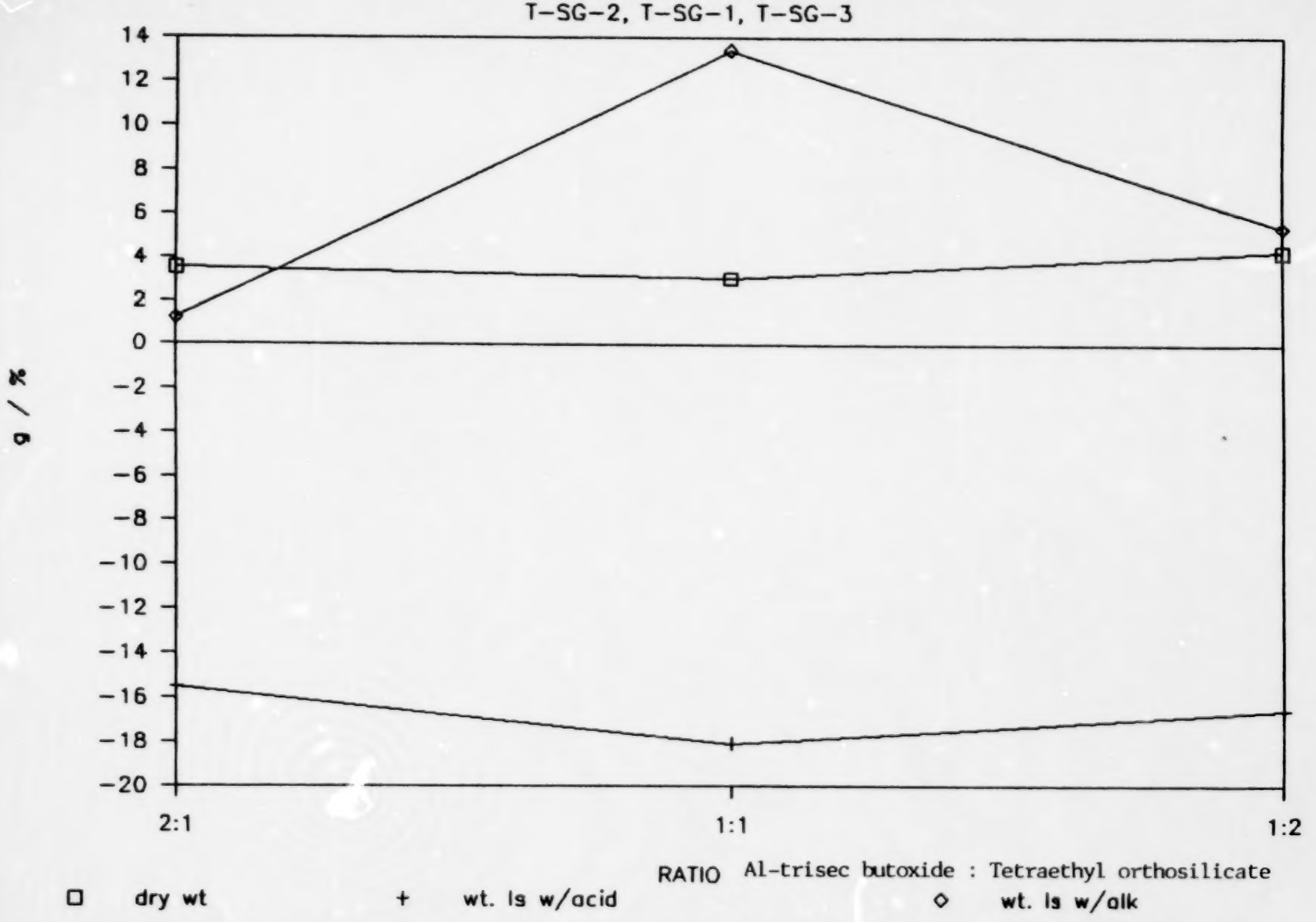


Fig. 1. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in%) and weight loss in 30% sodium carbonate solution (wt ls w/alk in%) as functions of the ratio of Al-trisec butoxide to tetraethyl orthosilicate with 2 ml addition of 10% ammonia water (Formulation A)

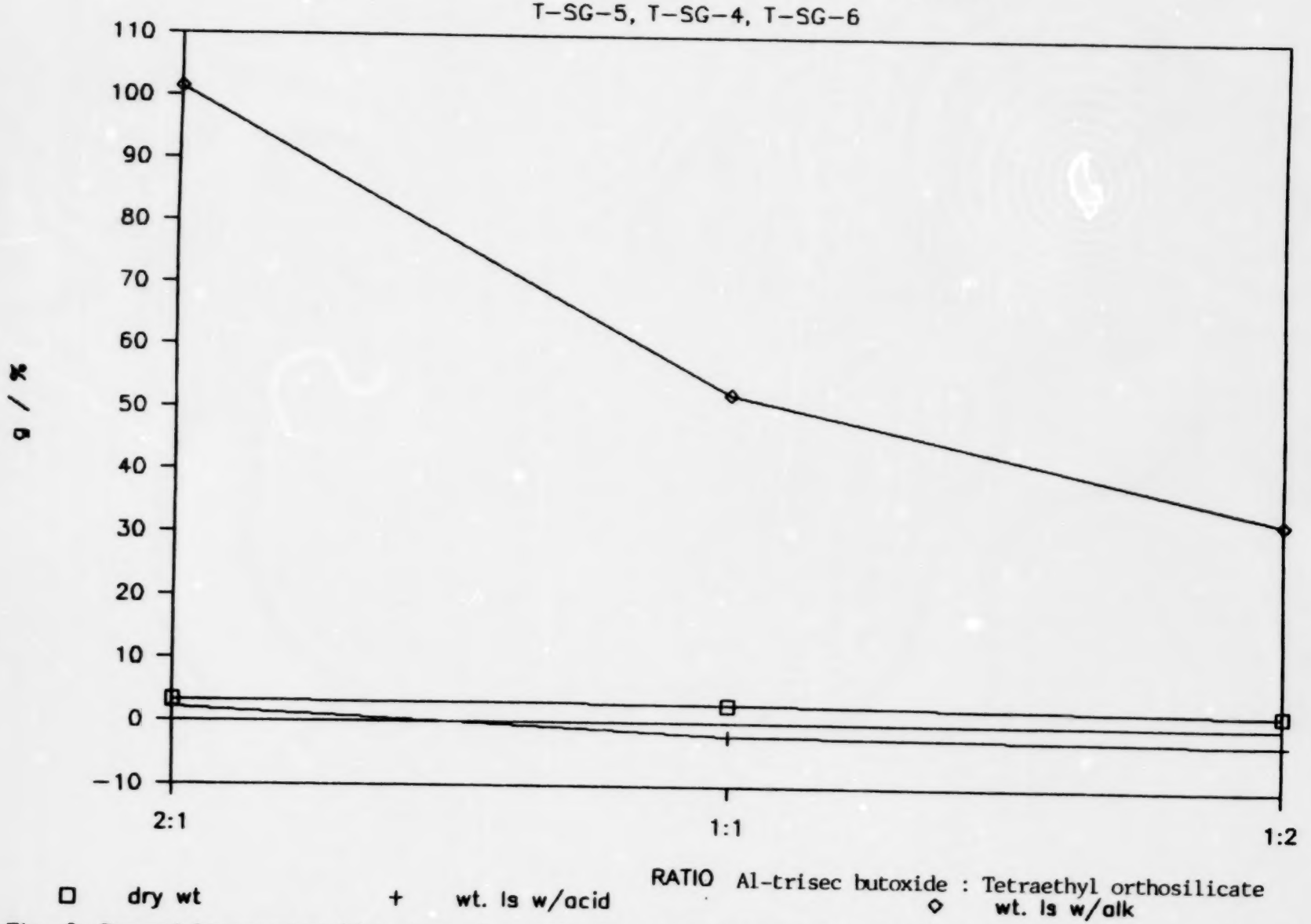


Fig. 2. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk in %) as functions of the ratio Al-trisec butoxide to tetraethyl orthosilicate with 30 ml addition of 1% ammonia water (Formulation A).

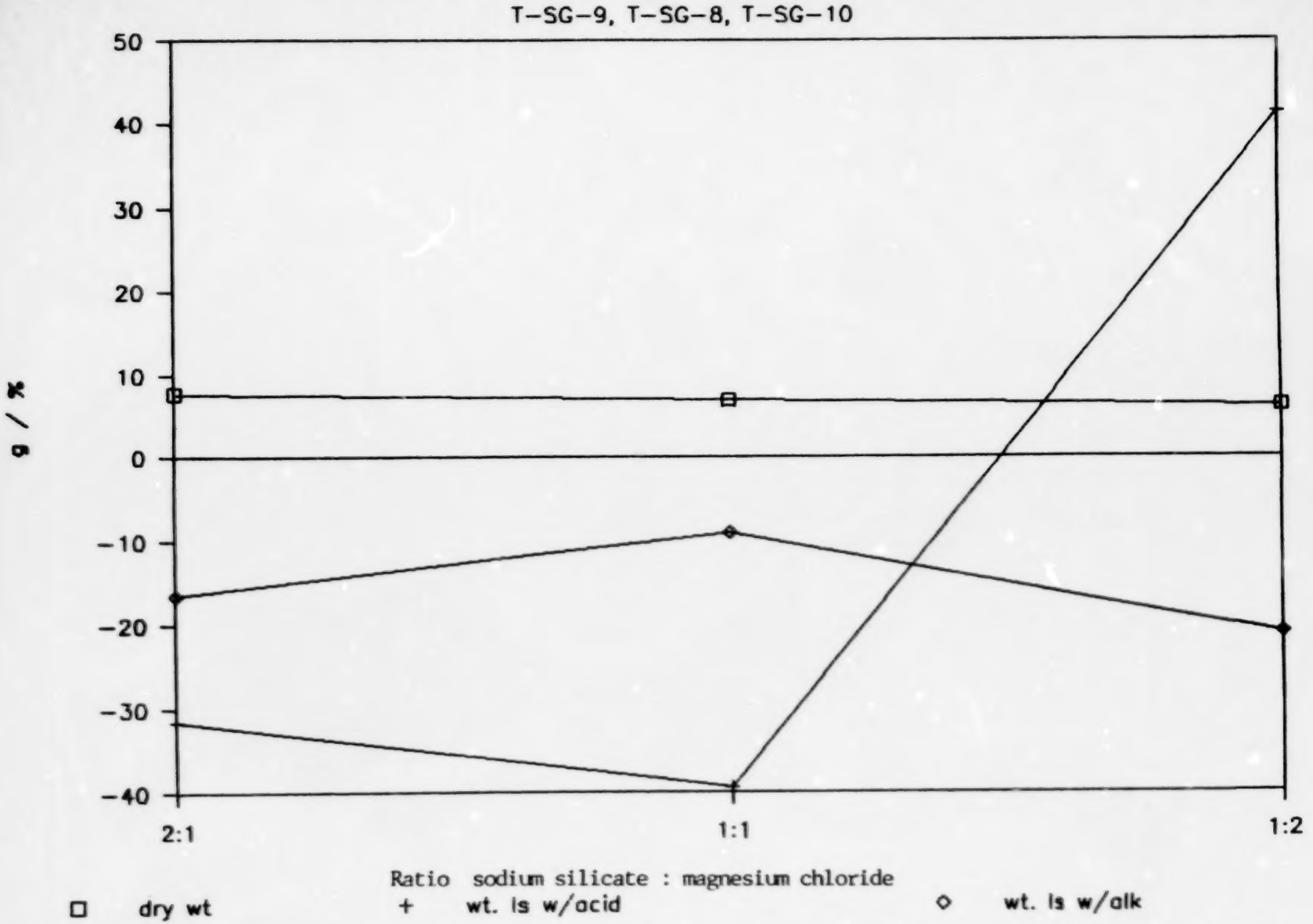


Fig. 3. Dry weight recovery (dry wt in g), weight loss in pH 2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk) as functions of the ratio sodium silicate to magnesium chloride with 15 ml addition of 10% ammonia water (Formulation B).

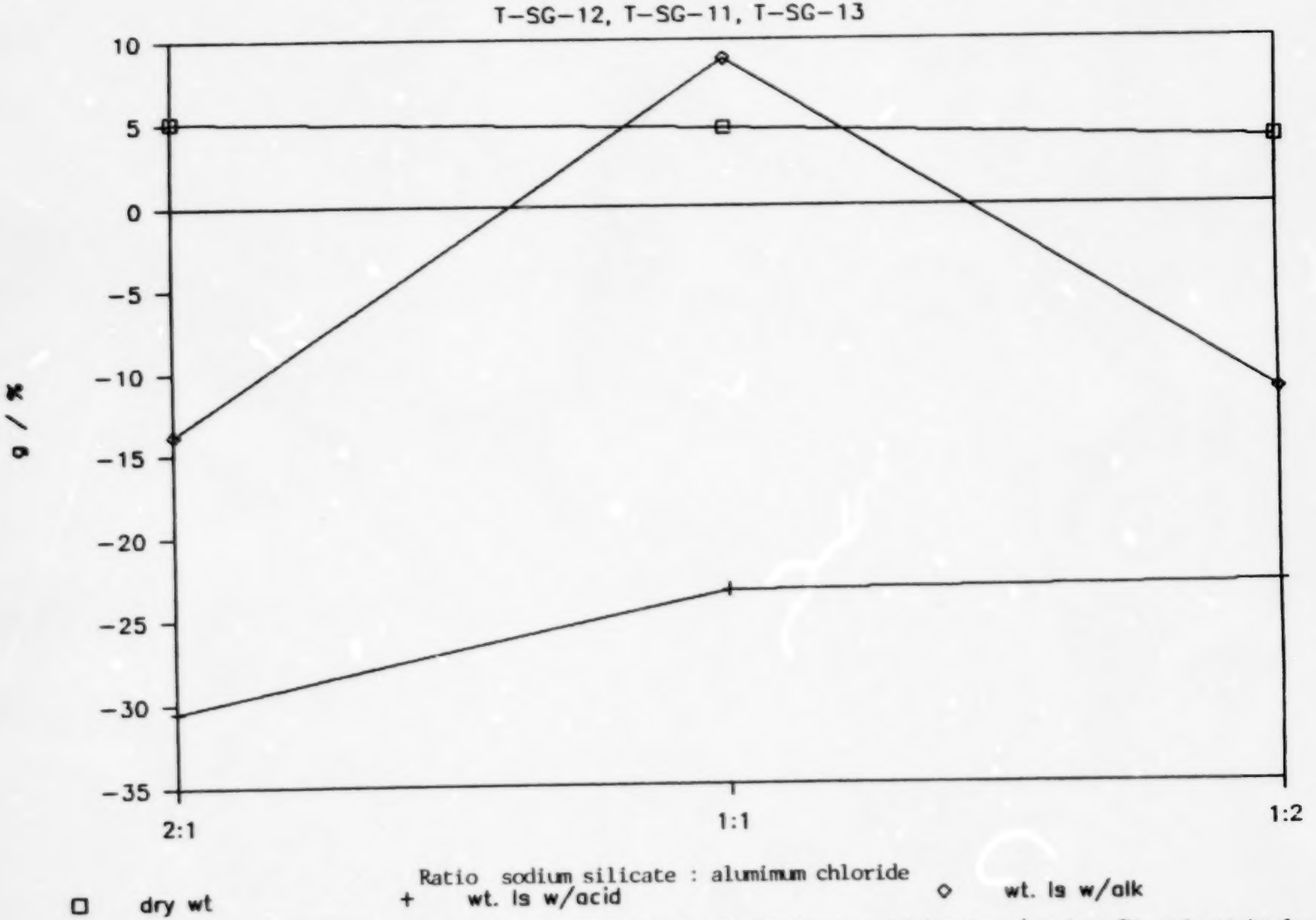


Fig. 4. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk in%) as functions of the ratio sodium silicate to aluminium chloride with 15 ml addition of 10% ammonia water (Formulation C).

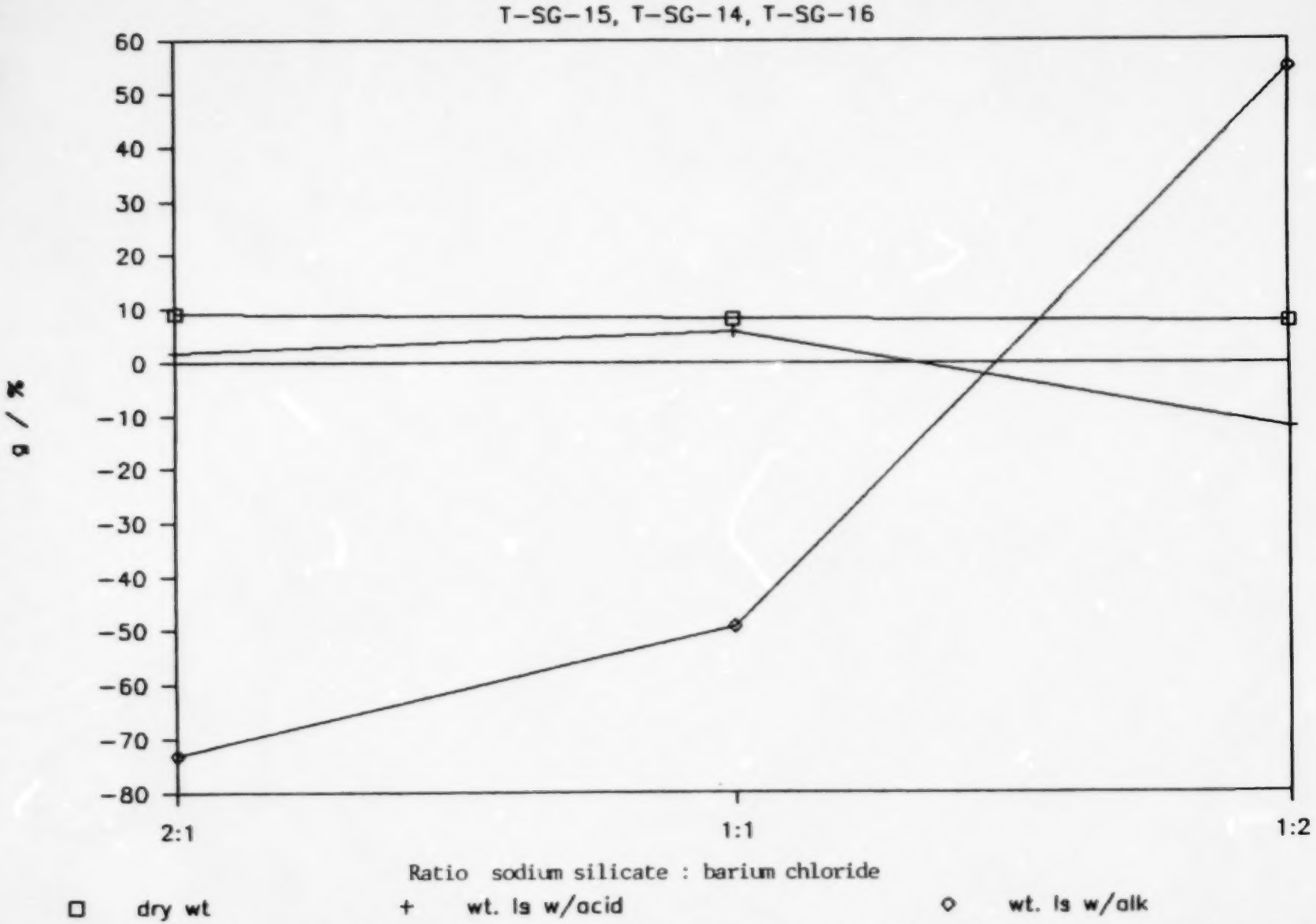


Fig. 5. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk in %) as functions of the ratio sodium silicate to barium chloride with 15 ml addition of 10% ammonia water (Formulation D).

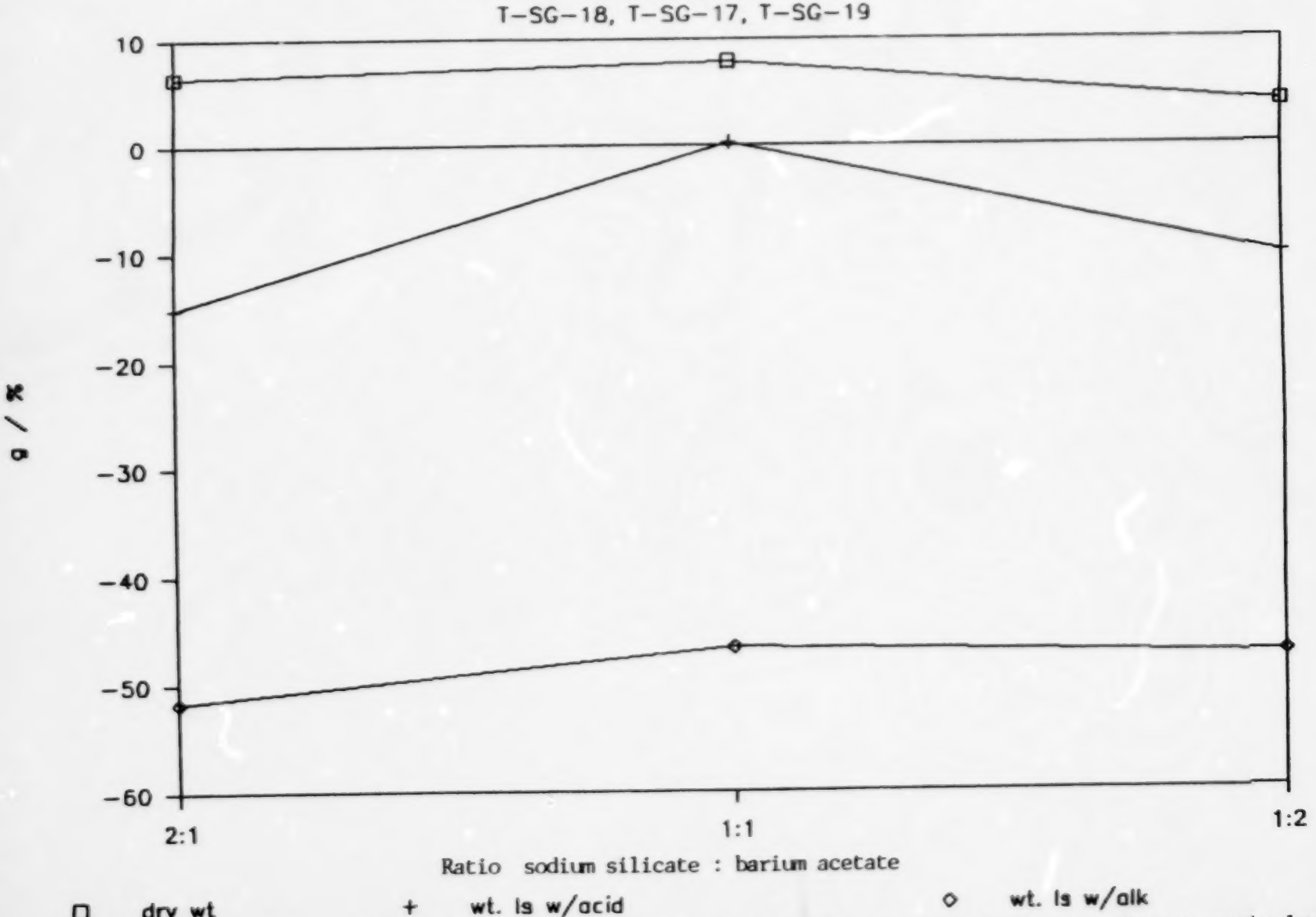


Fig. 6. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk in %) as functions of the ratio of sodium silicate to barium acetate with 15 ml addition of 10% ammonia water (Formulation E).

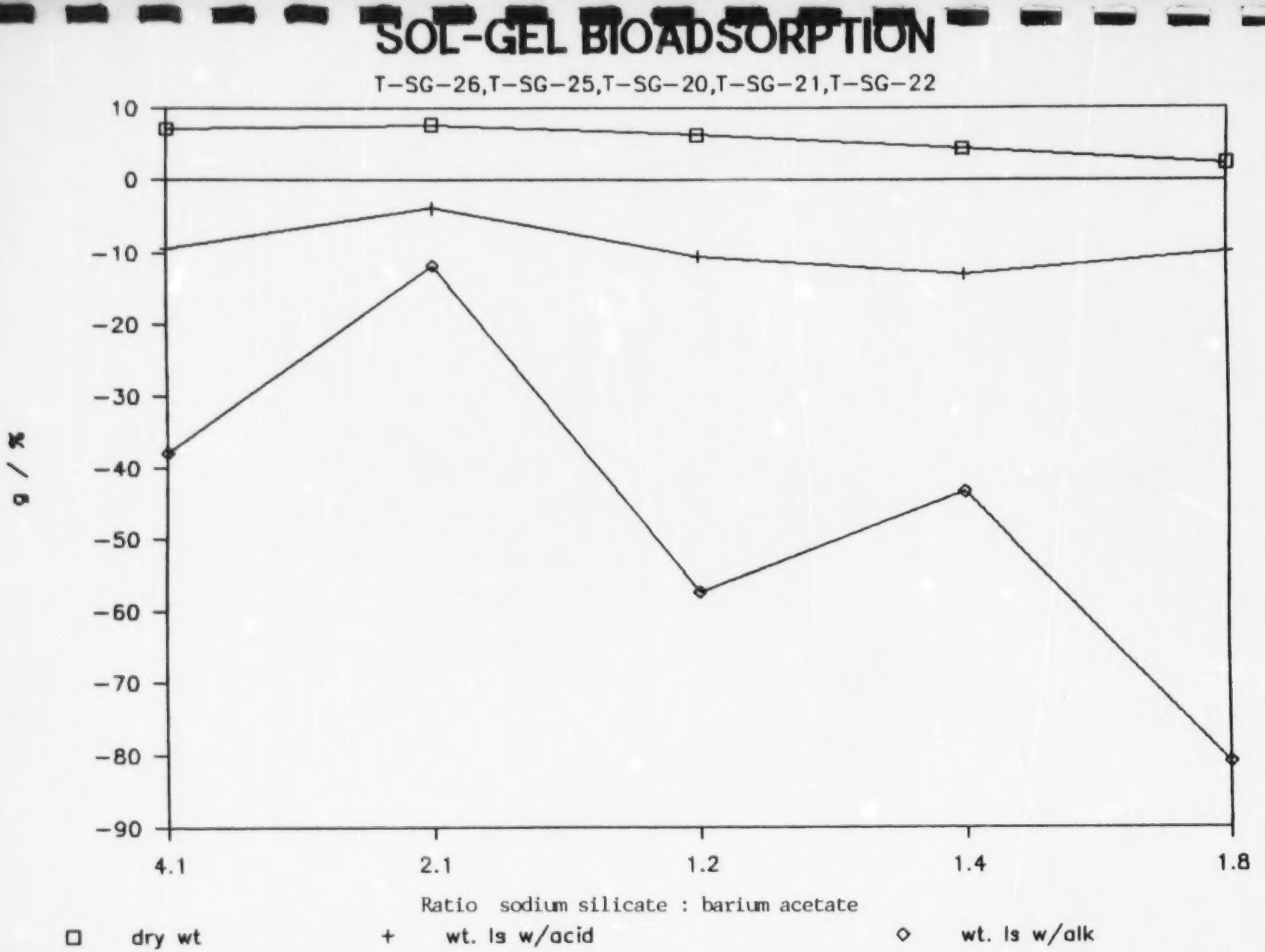


Fig. 7. Dry weight recovery (dry wt in g), weight loss in pH2 sulphuric acid (wt ls w/acid in %) and weight loss in 30% sodium carbonate solution (wt ls w/alk in %) as functions of the ratio sodium silicate to barium acetate with 15 ml addition of 10% acetic acid (Formulation F).

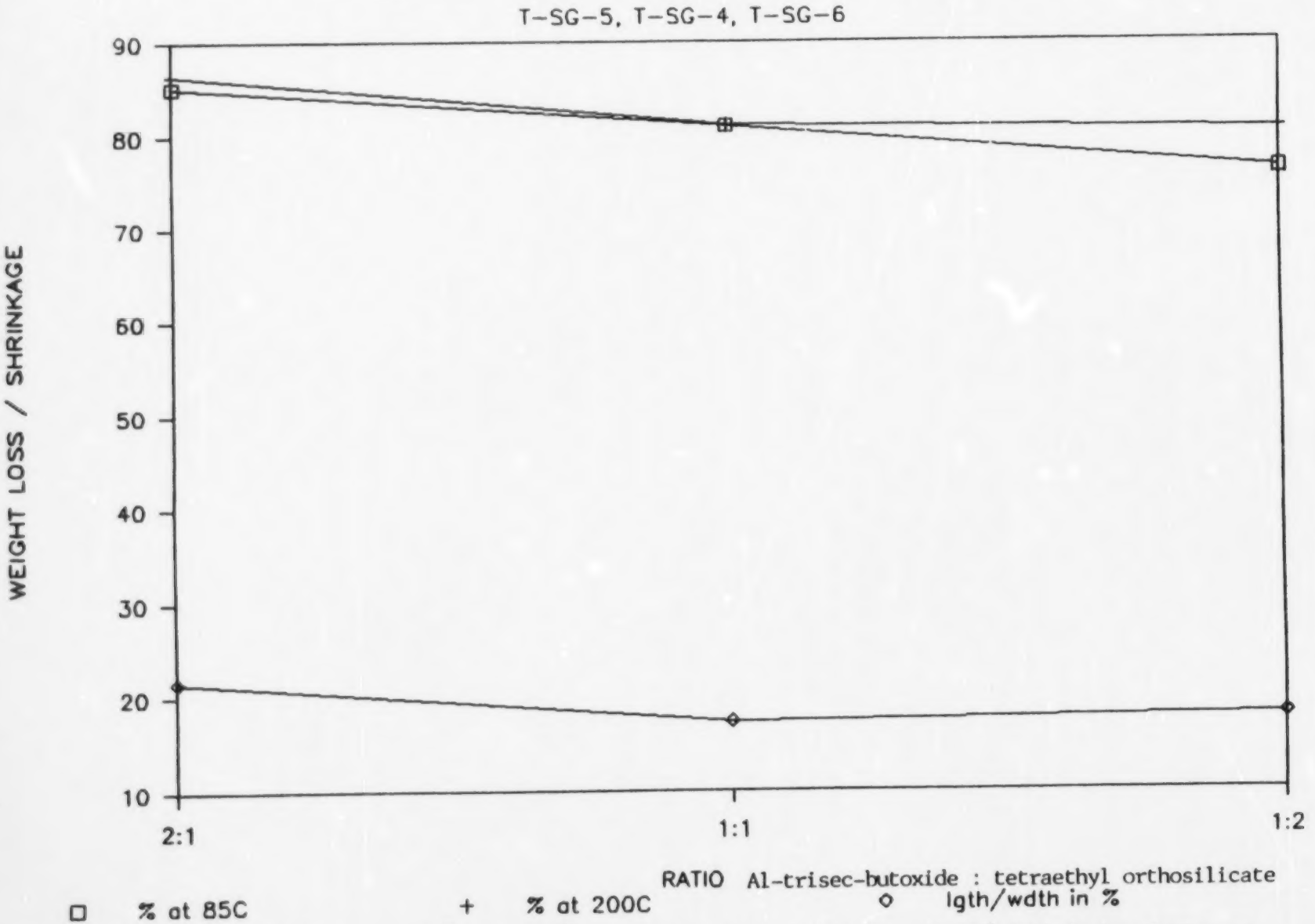


Fig. 8. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lgth/wdth) during drying as functions of the ratio aluminium trisec-butoxide to tetraethyl orthosilicate (Formulation A).

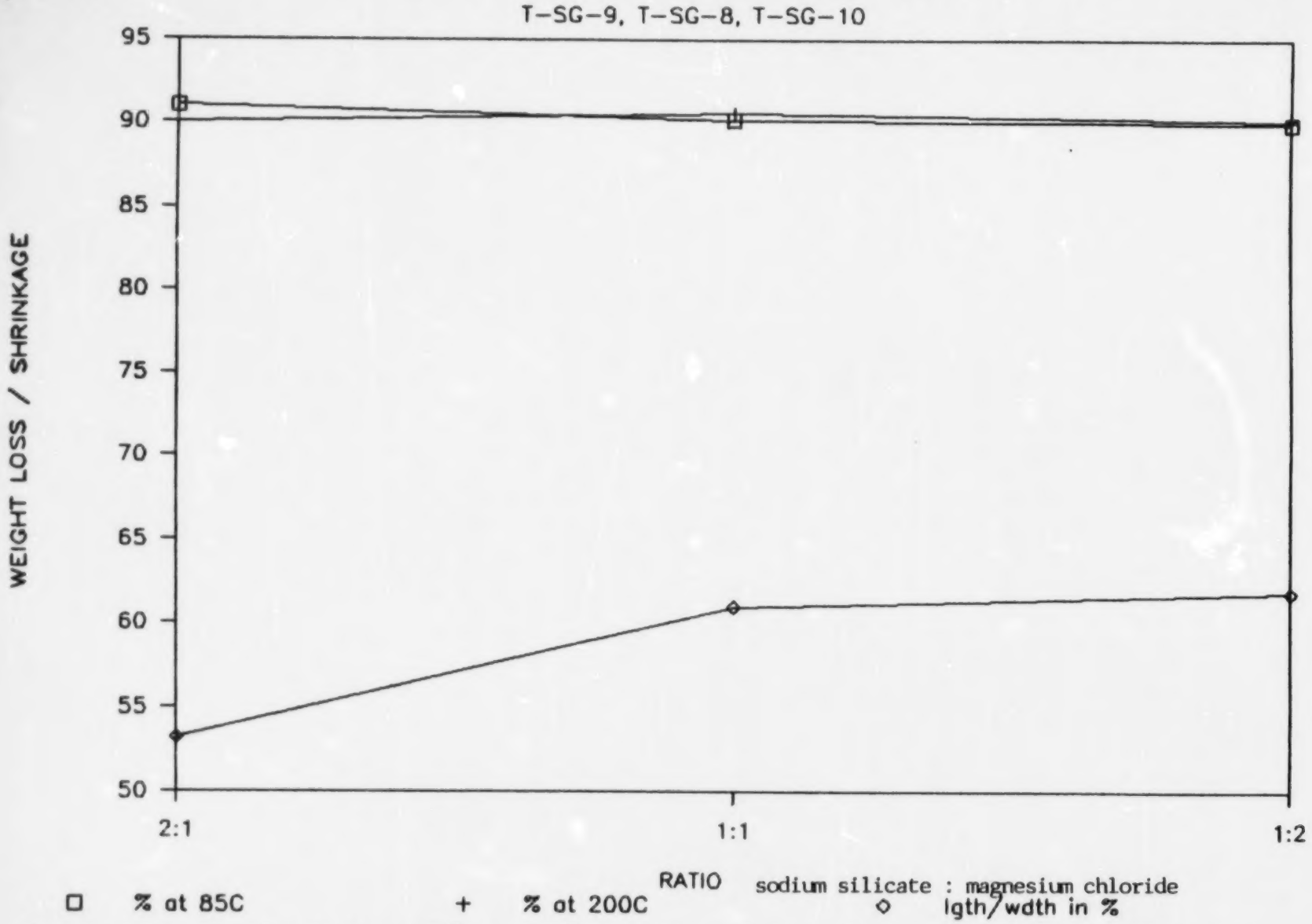


Fig. 9. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lgth/wdth) during drying as functions of the ratio sodium silicate to magnesium chloride (Formulation B).

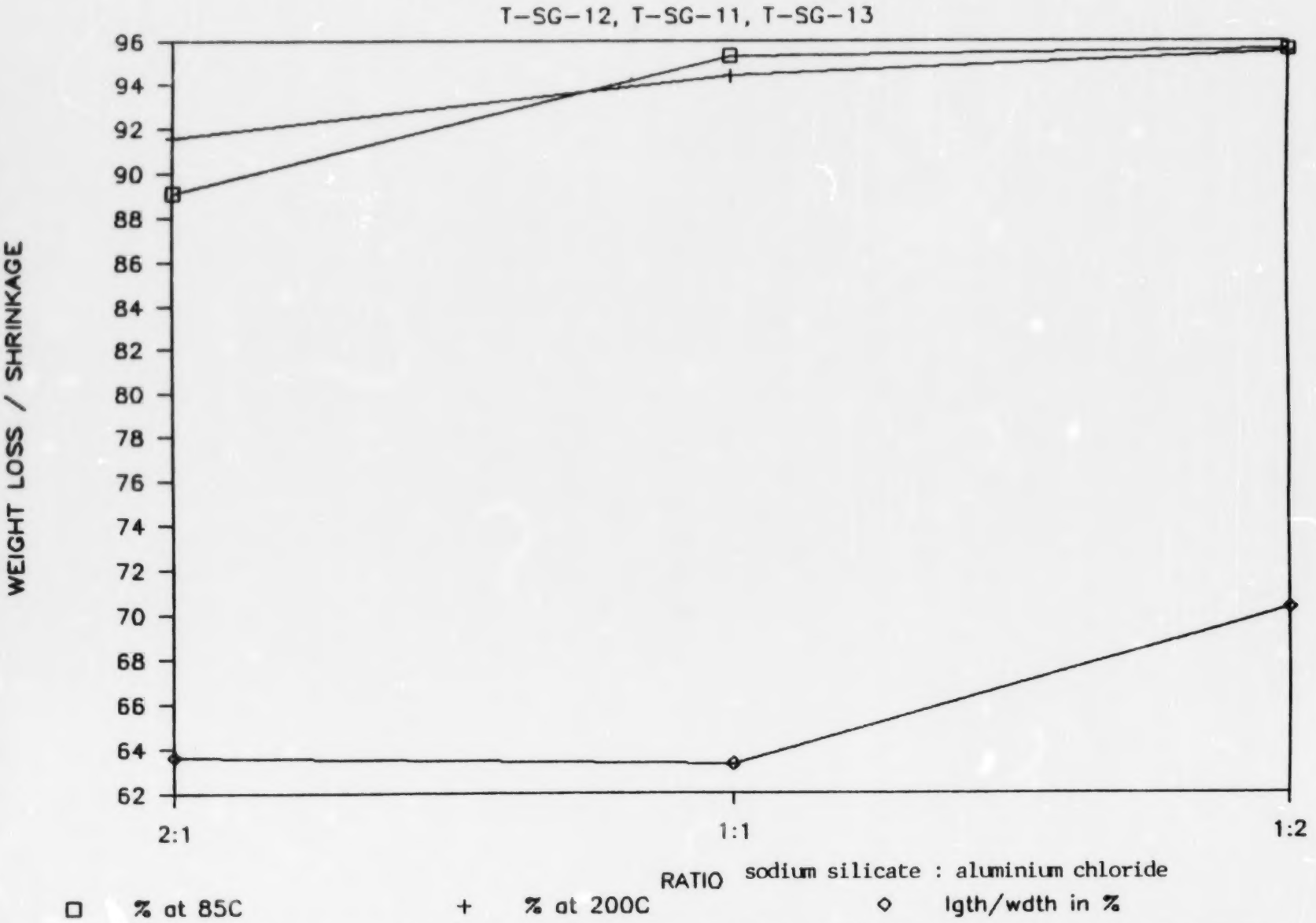


Fig. 10. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lght/wdth) during drying as functions of the ratio sodium silicate to aluminium chloride (Formulation C).

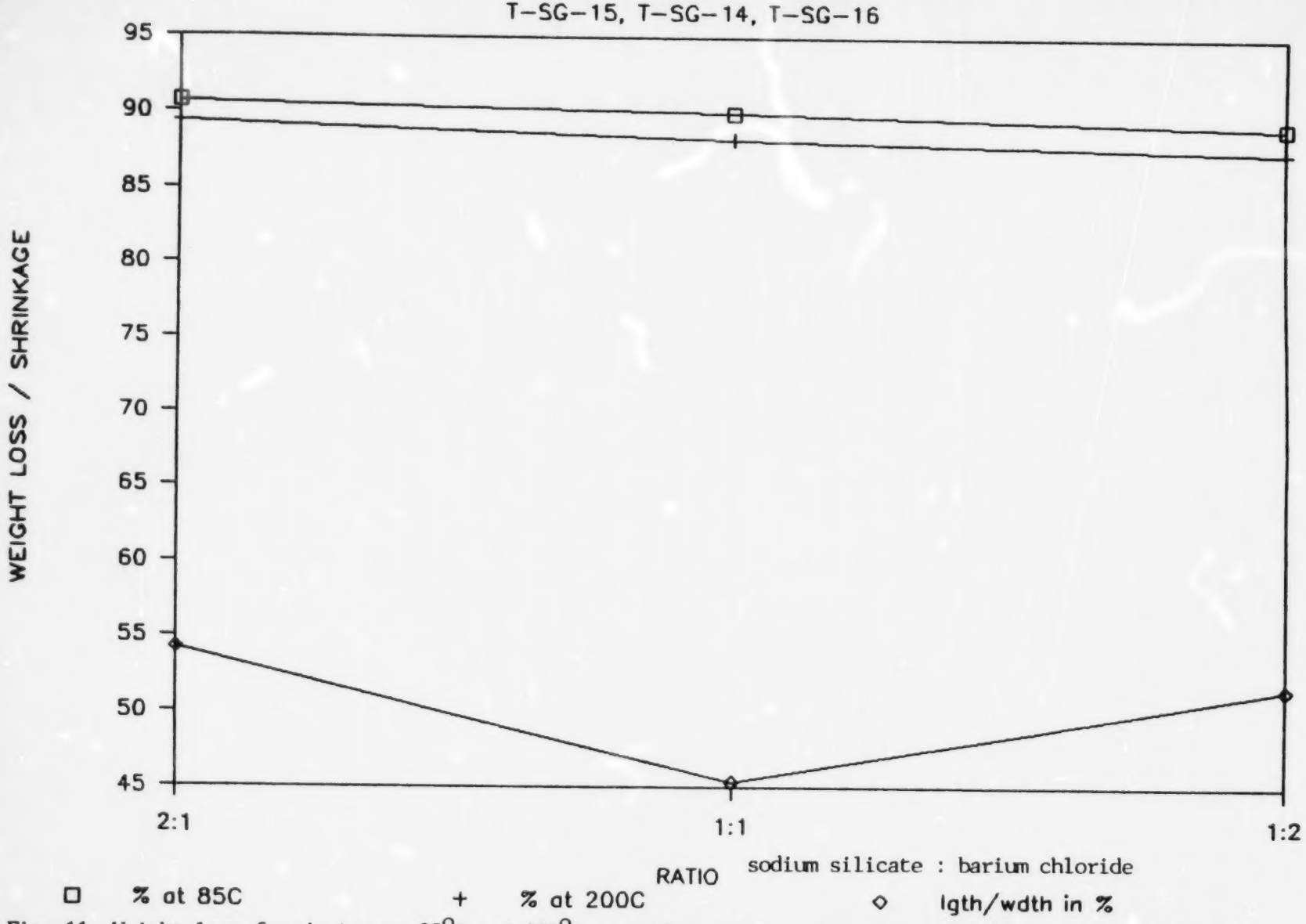


Fig. 11. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lght/wdth) during drying as functions of the ratio sodium silicate to barium chloride (Formulation D).

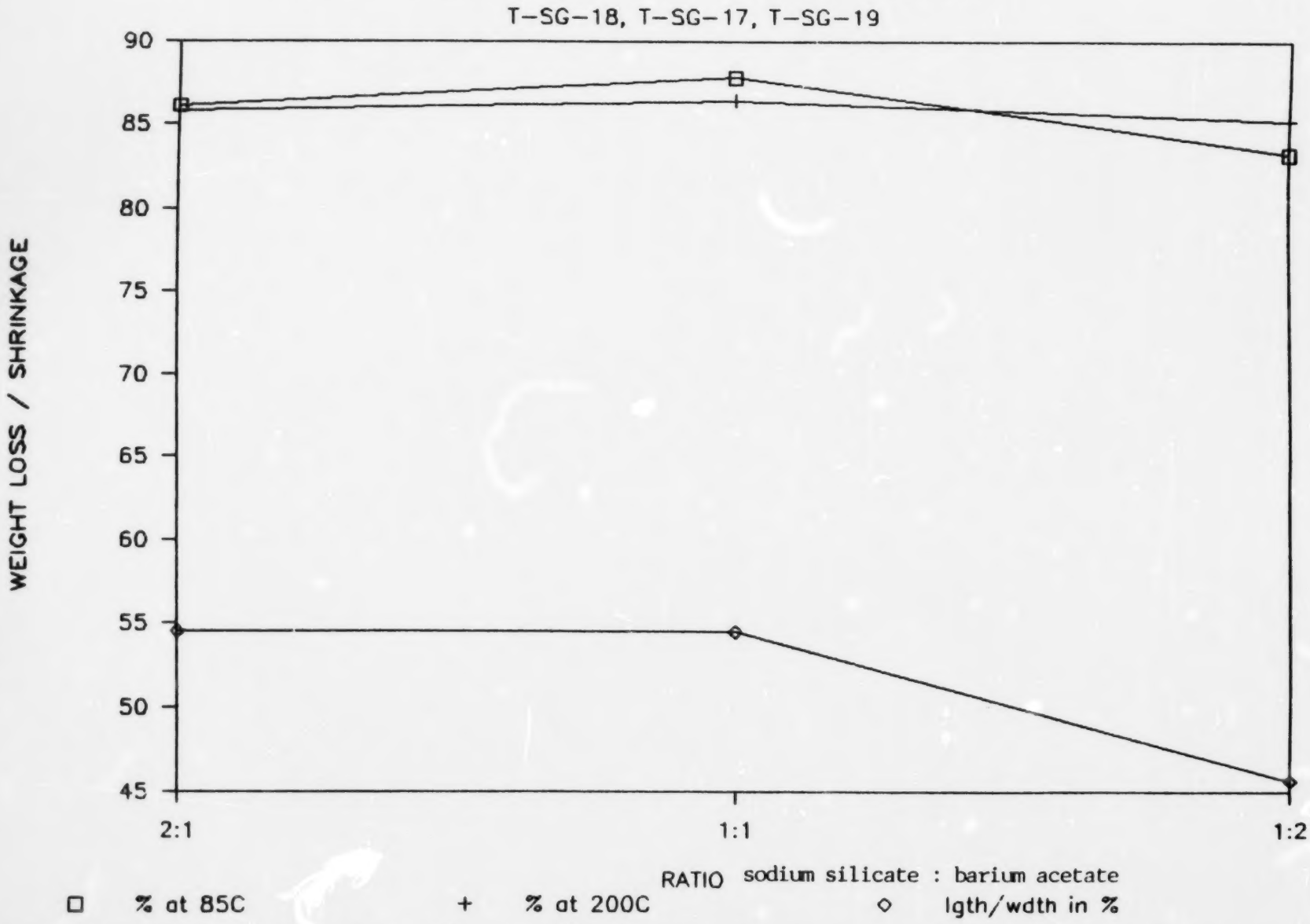


Fig. 12. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lght/wdth) during drying as functions of the ratio sodium silicate to barium acetate (Formulation E).

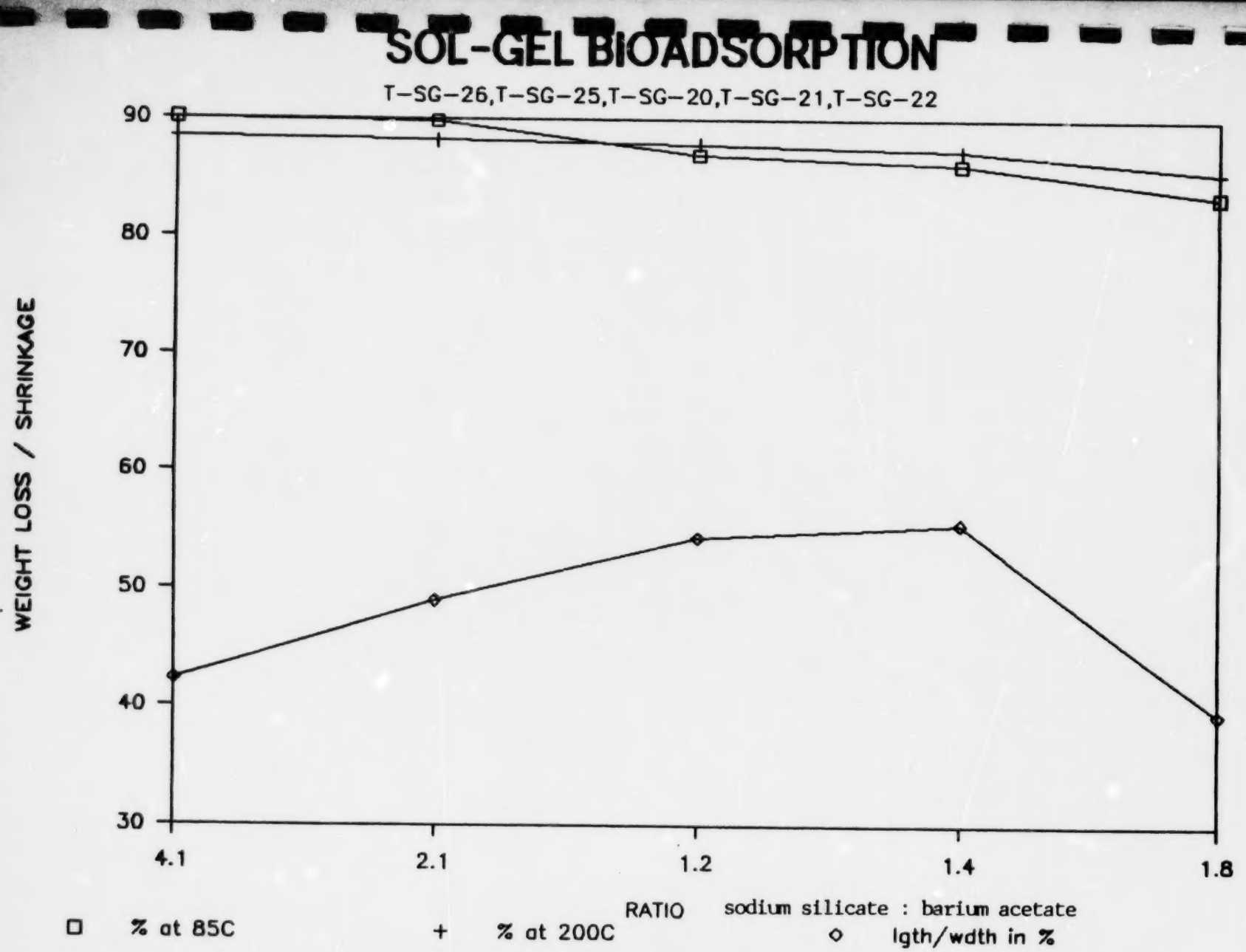


Fig. 13. Weight loss for drying at 85°C and 200°C as well as linear shrinking (lght/wdth) during drying as functions of the ratio sodium silicate to barium acetate (Formulation F).

Fig. 14 Loading behaviour of sol-gel biomass type I and II (tests 1 to 4, flowrate 0.7 L/hr = 70 BV/hr).

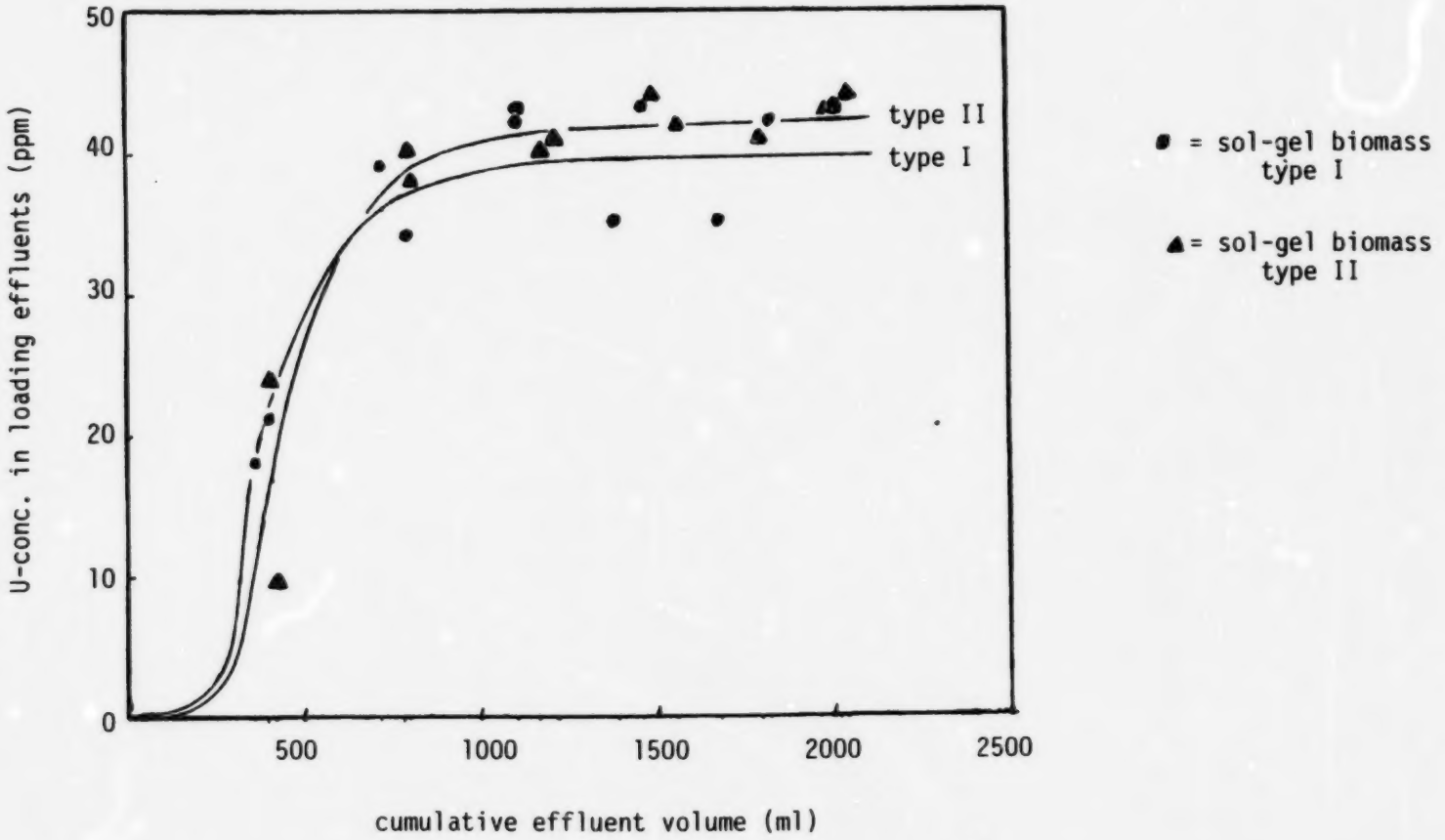


Fig. 15 Loading behaviour of sol-gel biomass type II (test 5, flowrate 0.47 L/hr = 47 BV/hr).

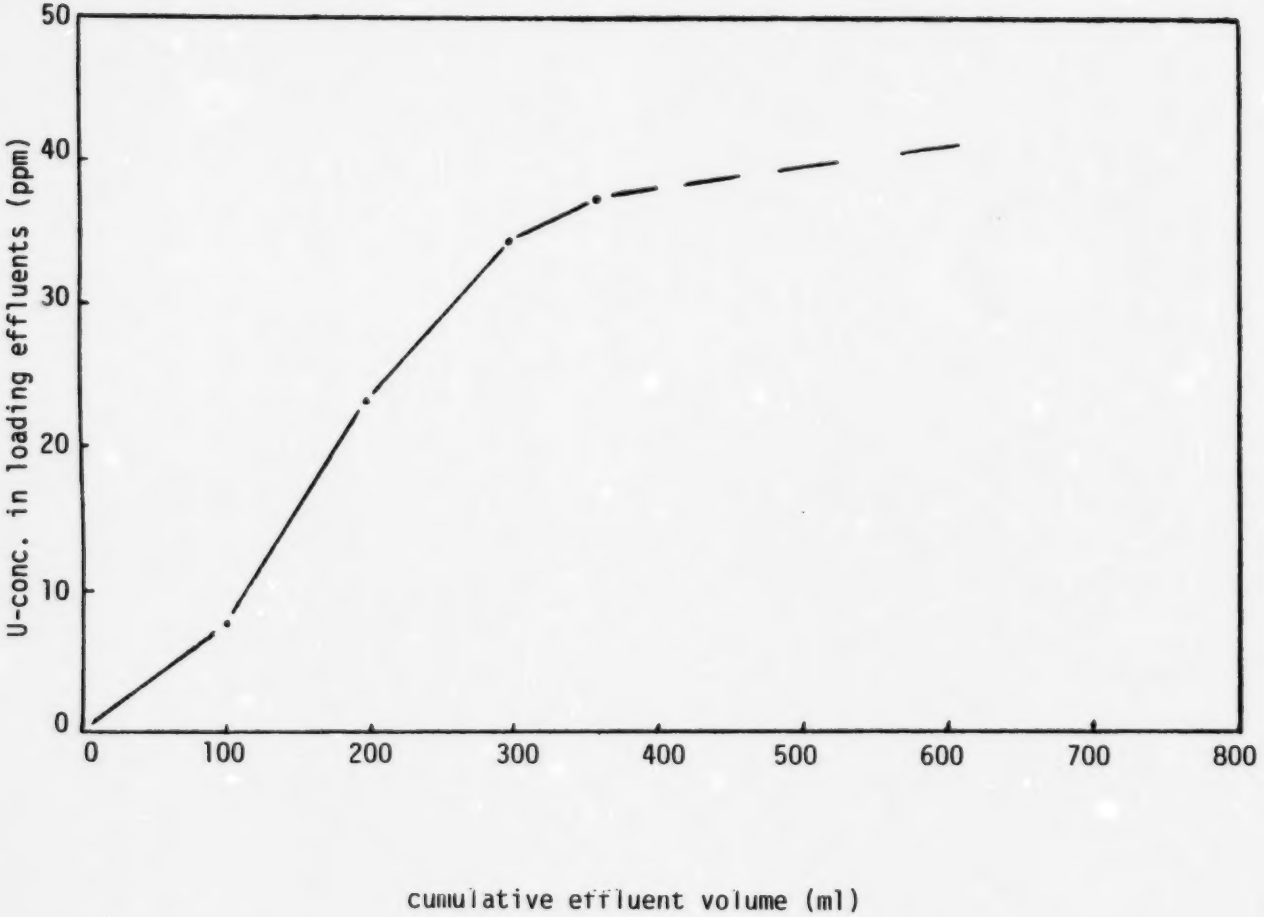
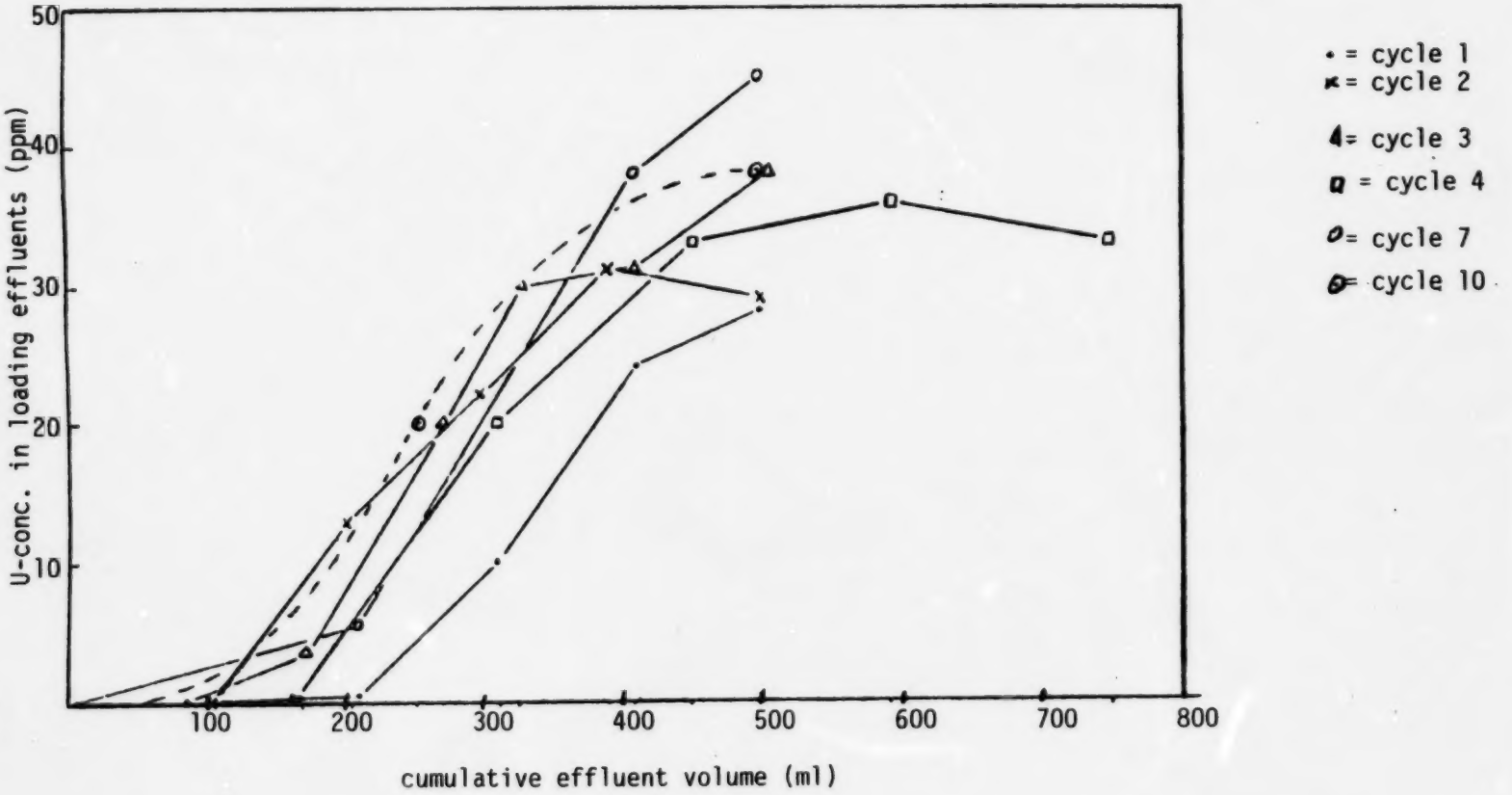


Fig. 16 Loading behaviour of sol-gel biomass type III (test 9, flowrate 0.47 L/hr = 40 BV/hr).



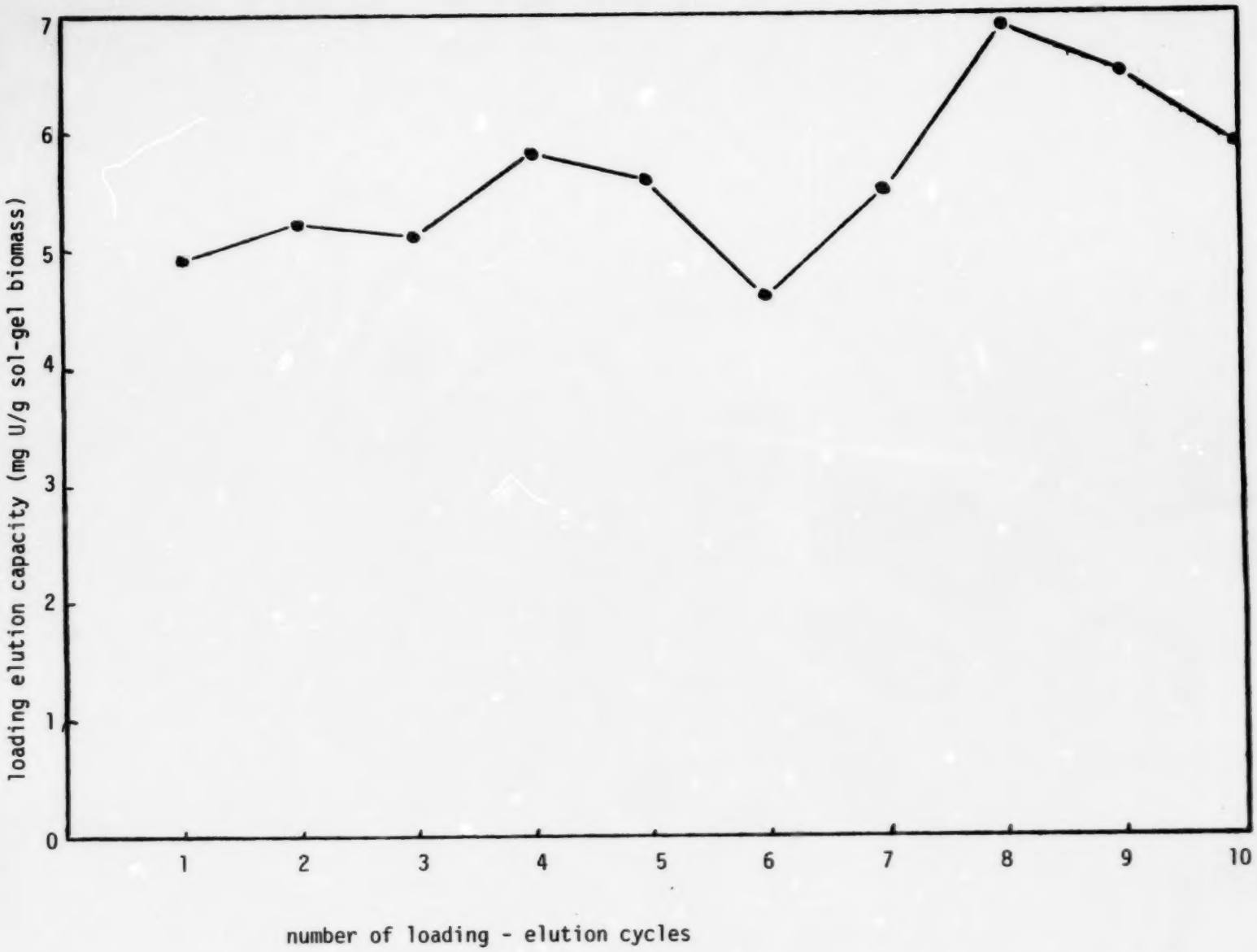


Fig. 17 Loading elution capacity of sol-gel biomass type III for an average throughput of 500 ml (50 BV) minewater as function of number of cycles (test 9).

Fig. 18 Eluting behaviour of sol-gel biomass type III (test 9).

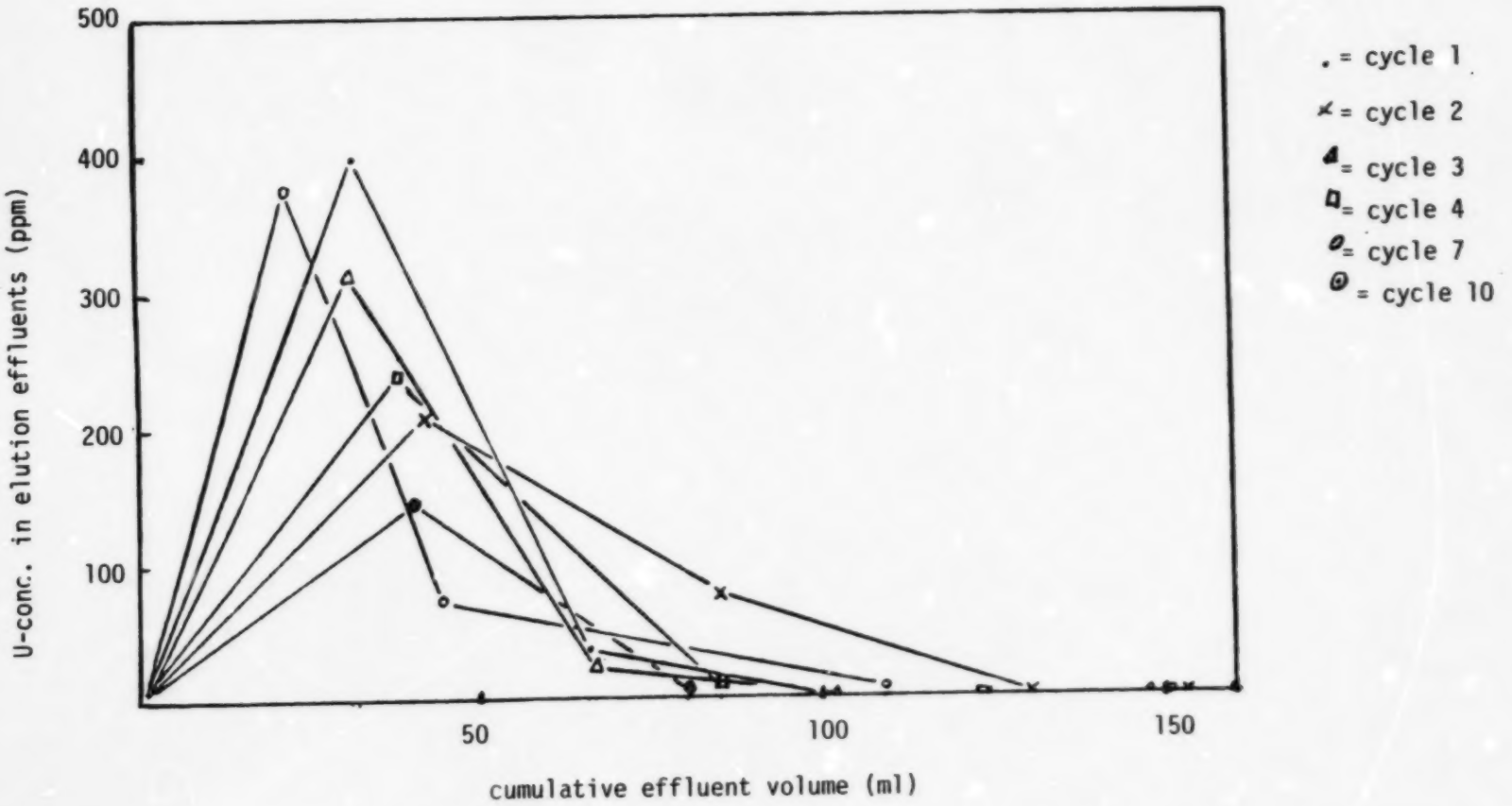
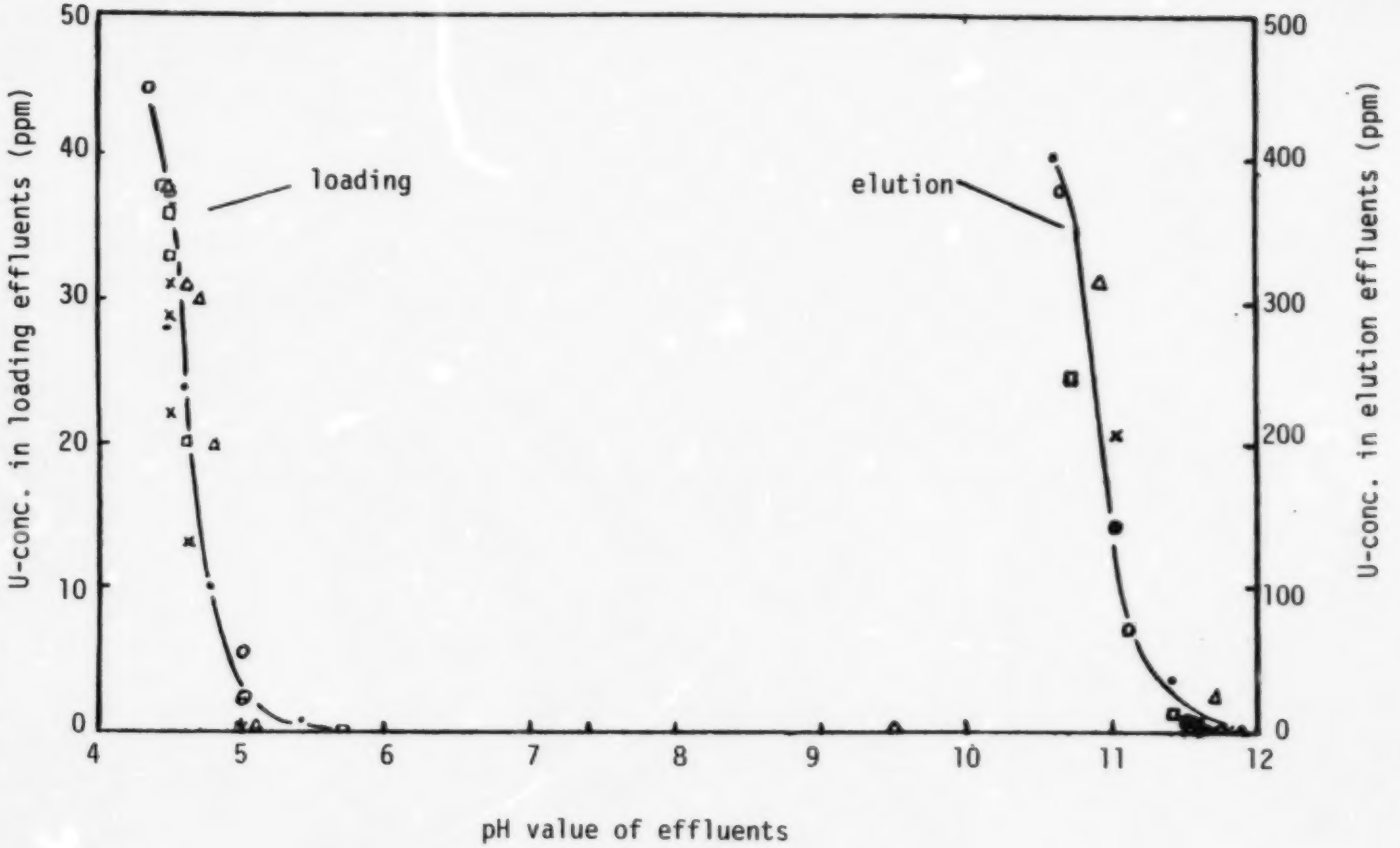


Fig. 19 Uranium concentrations of the effluents from loading and eluting sol-gel biomass type III as a function of the pH value (test 9).



APPENDIX:

Biomass Production

June 2, 1988

Attention: Ian Todd
Pilot Plant

Report No.: 88-48-65000-006

Identification: W.O. # 30290

Specifications of Order: Generate Inactivated Biomass from Acidophilic *Penicillium* Species

---

INTRODUCTION

The objective of this task was to produce inactivated Penicillium biomass according to the final growth conditions used in a previous study with Acres, Davy, and McKee. The organism would be cultivated in a proprietary medium supplied to the section by Dr. M. Tzesos, McMaster University. The medium would be supplied as a frozen concentrate which would be thawed in our laboratory and diluted to the appropriate volume immediately prior to autoclaving.

PROCEDURE

The medium concentrate was received from Dr. Tsezos and stored frozen until required. It was received in five bottles (4L of concentrate per bottle).

Generate Inactivated Biomass from
Acidophilic Penicillium Species
For: Pilot Plant

The contents of one bottle were thawed and mixed well prior to sampling. An aliquot (400 mL) was diluted to 1L with distilled water and divided into 150 mL volumes in 500 mL baffled culture flasks. The flasks plus contents were sterilized by autoclaving at 121°C for fifteen minutes. The cooled, sterile medium was inoculated with spores of the acidophilic Penicillium sp. taken from slants stored at 4°C. The cultures were incubated with shaking at room temperature.

Growth, based on visual observation, was slower than expected, but after 72 hours, two of the cultures (300 mL) were used to inoculate 5L of sterile medium prepared from the concentrate. This medium was also diluted 2 volumes to 5 volumes with distilled water and was sterilized in a 7.5 fermenter for 45 minutes at 121°C. The culture was then incubated at room temperature with mechanical agitation (400 rpm) with baffled paddles and aeration (2L per minute) through a sparger located beneath the lowest paddle. The culture was sampled aseptically at selected intervals based on the apparent growth of the culture. Biomass concentration was determined by filtering an aliquot through a preweighed pad of cheesecloth and washing it well with warm tap water until essentially free of medium. The washed biomass was dried in vacuo at 50°C and the weight of the pad plus biomass, was determined.

It was observed that whereas the growth of the Penicillium was somewhat slow in the small shake cultures, it was negligible after 96 hours' incubation in the larger culture. Biomass which had been formed at this time had stunted morphology and was not satisfactory in appearance. No change of pH was noted.

Based on these observations, it would appear that degradation of the medium as had been observed in the earlier study with sterile medium supplied by Dr. Tzesos was now occurring when the non-sterile concentrate was diluted and autoclaved in our laboratory using short sterilization times. Autoclaving caused the medium to darken, most noticeably in the case of the bulk medium which was autoclaved for 45 minutes and required longer depressurization and cooling periods.

The explanation for this difference in the behaviour of the medium was not obvious. It was noted that the pH of the diluted medium was 3.8 compared with 4.2 in the successful cultures in the previous study. Accordingly, the batch tests were repeated using diluted medium which was adjusted to pH 4.3 with sodium hydroxide solution prior to autoclaving for 15 minutes. The medium still darkened and when inoculated with spores of the Penicillium, there was still a significant lag time in the growth of the fungal mycelium.

In a second test, the pH was adjusted to 5.0 prior to autoclaving, and when autoclaved and inoculated with the Penicillium, growth of the fungal mycelium was satisfactory. However, when the medium was autoclaved for 45 minutes as for the bulk medium in the fermenter, the degree of darkening of the medium was still severe (little difference for previous unsuccessful tests).

Eventually, successful culturing of the Penicillium sp. was obtained in 5L cultures, by diluting the concentrate as per instructions and adjusting the pH to 5.0 with sodium hydroxide solution. The medium was divided into three volumes of 1.0 - 2.0 L in large (6L) Erlenmeyer flasks and then autoclaved for only 20 minutes at 121^{o}C. The medium was removed from the autoclave as soon as possible in order to minimize the time that it was exposed to the elevated temperatures. Some slight darkening of the medium was still noted but when the sterile medium was transferred aseptically to the 7.5L fermenter (which had been sterilized separately) and inoculated with 300 mL of Penicillium culture, the growth of the fungal mycelium was rapid and based on the change of pH (typically 4,8 → >5.0) was completed in less than 40 hours. This matched the successful culture with previous study.

The Pencillium biomass was harvested as soon as an increase was noted in the pH of the medium. The biomass was filtered through cheesecloth and washed extensively with warm tap water. It was then resuspended in warm tap water and again filtered. In this way, much of the residual nutrients from the medium were washed off the biomass.

Generate Inactivated Biomass from
Acidophilic Penicillium Species
For: Pilot Plant

The biomass was inactivated by autoclaving at 121°C for 20 minutes and when cooled was immediately frozen. It was then freeze-dried.

SUMMARY

In total, approximately 300g of dried, inactivated Penicillium biomass have been produced.

Dr. J. Christison
Energy and Environmental
Engineering Division

JC/ss